PHOTOLYSIS AND ACID CATALYSED STUDIES OF SOME BIFUNCTIONAL SYSTEMS

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ABSTRACT

Reaction of 2-methyl-2-phenylprop-1-yl magnesium chloride(90) with benzaldehyde in tetrahydrofuran gives a 1:2 mixture of *meso*-and *dl*-2,7-dimethyl-2,4,5,7-tetraphenyl-octane-4,5-diol(91), 1,3-diphenyl-3-methylbutan-1-one(92a), benzyl alcohol(93), 2-methyl-2-phenylpropane(94) and 1,3-diphenyl-3-methylbutan-1-ol(97a). The mechanism involved in the formation of the products of the Grignard reaction is examined. The substituted 1-aryl-3-methyl-3-phenylbutan-1-ols(97b: *para*-methoxy, c: *para*-methyl, d: *para*-chloro, e: *meta*-chloro, f: 3',4'-dichloro) are prepared. Dehydration of the alcohols(97) with *p*-toluene-sulphonic acid and a short reaction time gives the *trans*-1-aryl-3-methyl-3-phenylbut-1-enes(88) but longer reaction times afford the 1-aryl-3,3-dimethylindanes(102) in a reaction involving intramolecular electrophilic substitution.

Short term photolyses of the *trans*-1-aryl-3-methyl-3-phenylbut-1-enes(88) give *cis*-1-aryl-3-methyl-3-phenylbut-1-enes(109) and *trans*-1-aryl-3,3-dimethyl-2-phenylcyclopropanes (112). Long term photolyses of the *trans*-alkenes(88) give 4-aryl-2-methyl-3-phenylbut-1-enes(115) in addition to the *cis*-alkenes(109) and *trans*-cyclopropanes(112). Deuterium labelling studies show that the secondary photoproducts(115) are formed by C1-C3 cyclopropyl bond cleavage. Photolyses of the *trans*-1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes(89) give the 1-aryl-3-methyl-3-phenylbutan-2-ones(139), 2-aryl-3-methyl-3-phenylbutanals(140) and secondary photoproduct hydrocarbons(141, 142, 143). Photolysis of 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144) gives benzophenone(46) and secondary photoproduct hydrocarbons(141, 145).

Photolysis of 2,3-diphenyl-1,2-epoxy-3-methylbutane(149) gives 2,3-diphenyl-3-methylbutanal(140), 2,3-diphenyl-3-methylbutan-1-ol(153), 3,3-diphenyl-4-hydroxyl-2-methylbut-1-ene(152) and 2,2-dimethyl-3,3-diphenyloxetane(151). Photolyses of a series of β,γ-unsaturated epoxides show both C-O and C-C bond cleavage of the epoxide ring. The interaction between the epoxide and vinyl moieties is discussed.

Reaction of the *trans*-1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes(89) with BF_3-etherate in benzene give 2-aryl-3-methyl-3-phenylbutanals(140) shown by deuterium labelling experiments to be formed by C1-O bond cleavage and alkyl migration, and the 1R*, 2R*-1-aryl-1-ethanoxy-3-methyl-3-phenylbutan-2-ols(189) in a process involving retention of configuration at C1. In ether as solvent the epoxides(89) give in addition to the aldehydes(140) and ethanoxyalcohols(189), 1-aryl-3-methyl-3-phenylbutan-2-ones (139), vinyl ethers(207) and dimers(208). The *cis*-1-aryl-1, 2-epoxy-3-methyl-3-phenylbutanes(216) react with BF_3-etherate in benzene to give the aldehydes(140) and ketones(139). 1,2-Epoxy-3-methyl-1,1,3-triphenylbutane(144) reacts with BF_3-etherate in benzene to give 2-phenylpropyl-2-(2,2-diphenylethylene)ether(217), 3-methyl-1,1,3-triphenylbutan-2-one(146), 2-phenylpropyl-2-ethylether(218) and benzophenone as primary products and 4-phenylpentan-2-ol(226) and 2,4-diphenyl-4-methylpent-1-ene(227) as secondary products. The chloro-substituted epoxide(230) gives 2-phenylpropyl-2-(2,2-bis-(4'-chlorophenyl)ethylene)ether(238) and bis-(4'-chlorophenyl)-ketone(235) as primary products and 2,4-diphenyl-4-methylpent-1-ene(227) as a secondary product on reaction with BF_3-etherate

in benzene. The complexity of the BF_3-etherate catalysed reactions of these systems(89, 144, 216, 230) is discussed.

INTRODUCTION

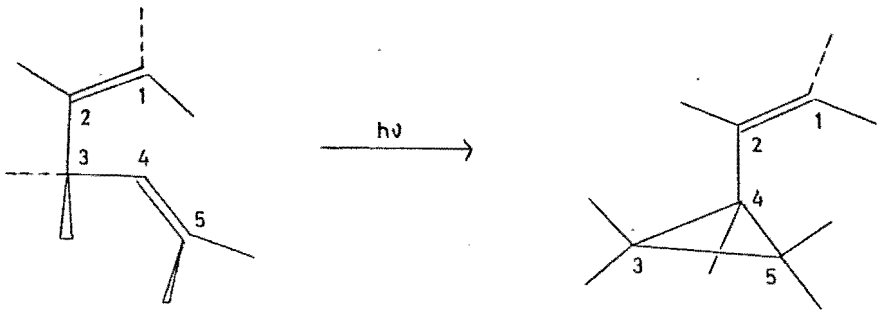
The work described in this thesis concerns a study of the reactions to light and to acid of a series of bichromophoric molecules in particular systems which contain an epoxide and unsaturated moiety, alkene or aryl. Systems of this type have received little attention. The photochemistry of 1,4-dienes and β,γ-unsaturated ketones has been studied and this work is briefly reviewed along with the photochemistry of some epoxide systems as a background for the present study. The second section of work reports the reaction of selected 3-aryl-1,2-epoxides with acid.

PART I

Photochemistry of Bichromophoric Systems

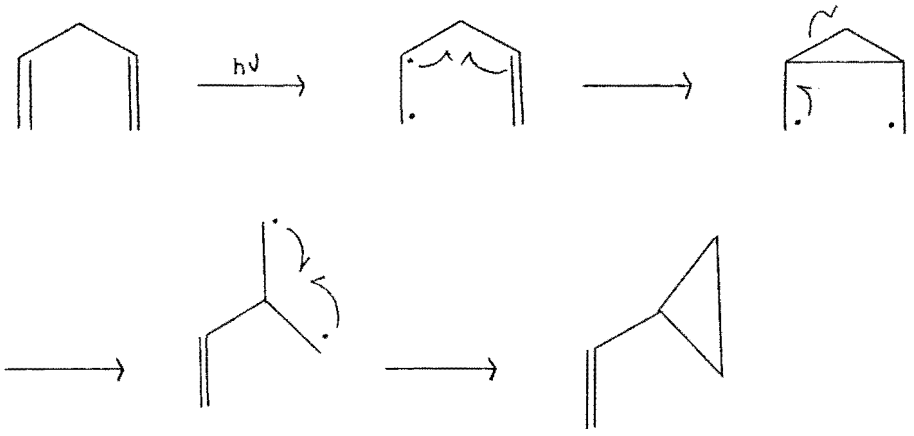
Organic photochemistry has matured to the stage where the consequences of excitation of the more common chromophores are reasonably well understood. The photochemical consequences of irradiating molecules containing two or more functional groups is more complex and has received detailed attention only recently. A knowledge of interchromophoric interactions and their dependence on separation and relative orientation is necessary to predict the photochemistry of even modestly complex organic structures. The interaction between functional groups may dominate a molecule's excited state chemistry.

Perhaps the most studied photochemical reaction of a bifunctional system is that of 1,4-dienes, a reaction known as the di-π-methane rearrangement, in which the 1,4-diene is converted into a vinyl-cyclopropane (Scheme 1).



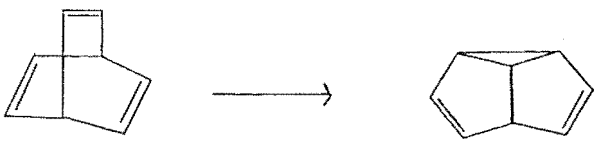
Scheme 1

The skeletal change in this rearrangement can be described by the mechanism shown in Scheme 2[1]. This reaction is



Scheme 2

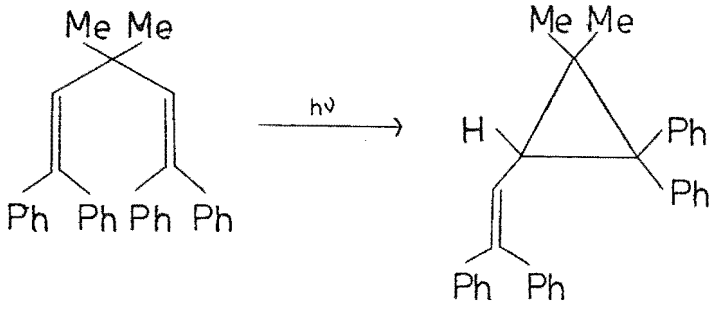
general for solution phase photolysis of acyclic, cyclic, bi- and tricyclic 1,4-dienes. One of the first examples of the di-π-methane rearrangement was found by Zimmerman and Grunewald[2] in the photochemical conversion of barallene(1) to semibullvalene(2), a reaction occurring with acetone as



(1) (2)

sensitiser.

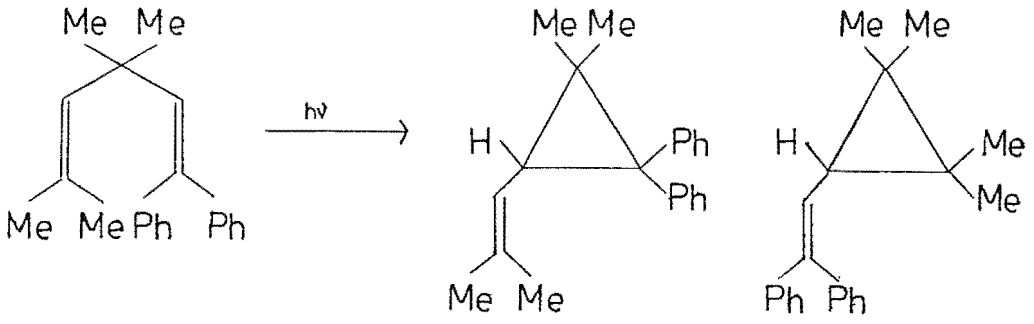
Phenyl substitution on a vinyl group facilitates direct excitation and rearrangement to the vinylcyclopropane occurs on irradiation without sensitisation. A classic and extensively studied example is the light-induced rearrangement of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene(3) to 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl) cyclopropane(4)[3]. In fact for this system sensitisation fails to produce the vinylcyclopropane product. Acyclic and



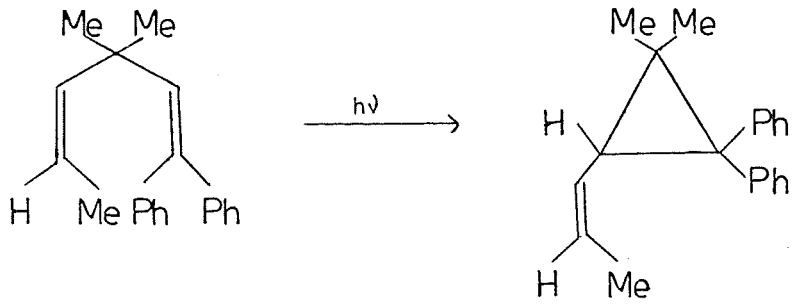
(3) (4)

monocyclic systems undergo the di-π-methane rearrangement only from the singlet manifold.

For unsymmetric 1,4-dienes,regiospecificity and stereoselectivity become important. 1,1-Diphenyl-3,3,5-trimethyl-1,4-hexadiene(5) for example rearranges to form



(5) (6) 100% (7) 0%



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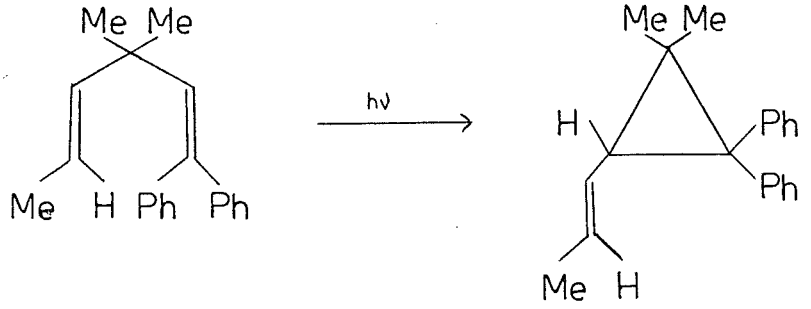
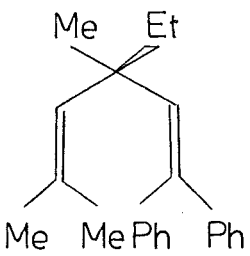
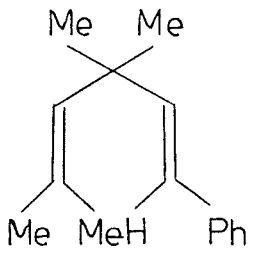


(9) (11)

only the photoproduct in which the phenyl groups are incorporated in the cyclopropane ring(6)[4]. Direct irradiation of *cis*- and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene(8,9) give the *cis*- and *trans*-cyclopropanes (10,11) respectively[5]. It is difficult to account for this stereospecificity by a mechanism which is generally depicted for simplicity as a stepwise rearrangement via diradical intermediates (Scheme 2). Furthermore, the di-π-methane rearrangement for (12) and (13) occurs with inversion of configuration at the 'methane' carbon (C_3)[6] and retention of configuration at Cl[7] respectively.

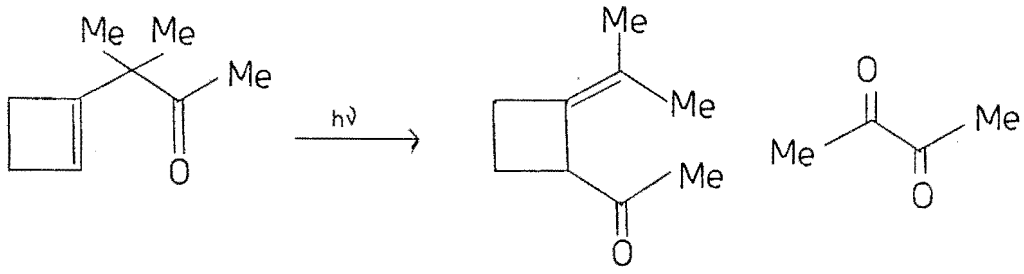


(12)



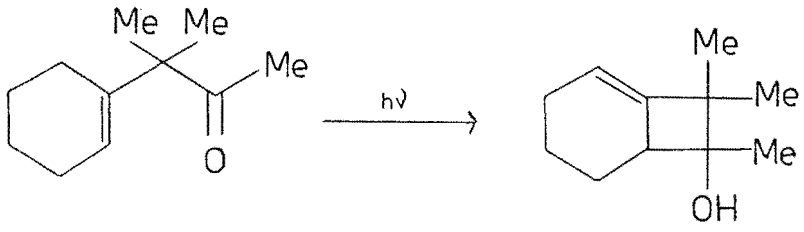
(13)

β,γ-Unsaturated ketones undergo photochemical reactions analogous to those of 1,4-dienes but their photochemistry is complex with many more reaction pathways being observed[1,8]. In addition to the normal photochemical rearrangements observed for ketones (cyclobutanol formation and decarbonylation), these unsaturated ketones also undergo transformations involving 1,3- and 1,2-acyl shifts. Minor structural changes have been observed to radically alter the observed photochemistry. For example, the cyclobutene system(14) undergoes 1,3-acyl migration to form (15) on direct irradiation and



(14) (15)

cyclobutanol formation is not observed[9]. The cyclohexene analogue (16) gives cyclobutanol (17) on direct irradiation



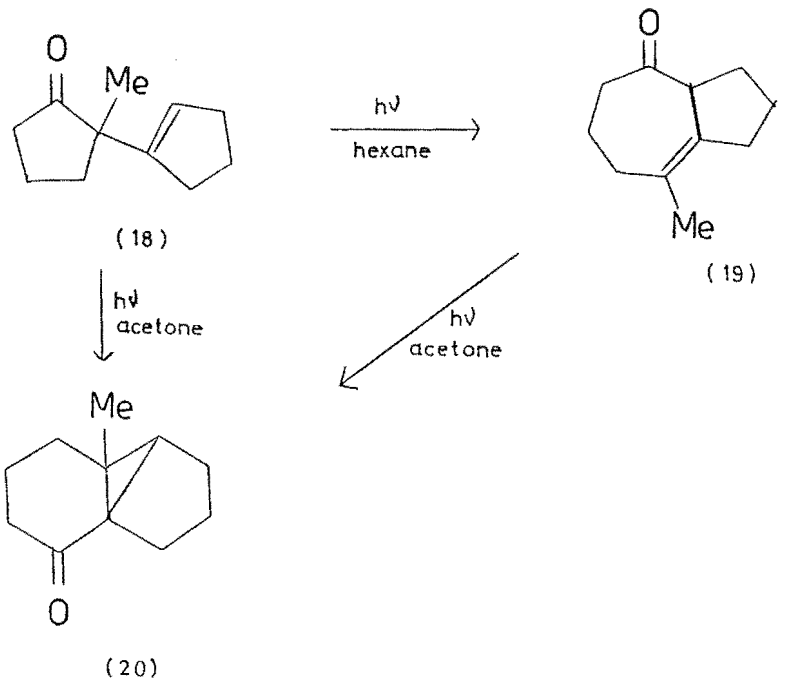
(16) (17)

and no 1,3-acyl migration is observed.

1,3-Acyl shifts occur from the lowest singlet excited state n,π* (S_1). The reactions are not quenched by triplet quenchers and are also not often observed in triplet sensitised reactions. In fact when 1,3-acyl migration occurs for

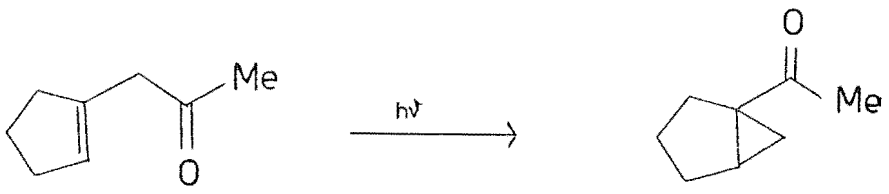
sensitised reactions[10,11] it has been proposed that the upper triplet excited state, $^3n,\pi^*$ (T_2) may be involved[12,13].

1,2-Acyl shifts (oxa-di-π-methane rearrangement) occur from the triplet excited state. Direct irradiation of 2-methyl-2-(cyclopent-1-enyl)cyclopentanone(18) gives hydroazulene(19) whereas the tricyclic ketone(20) is produced by a 1,2-acyl shift on direct irradiation in acetone[14].



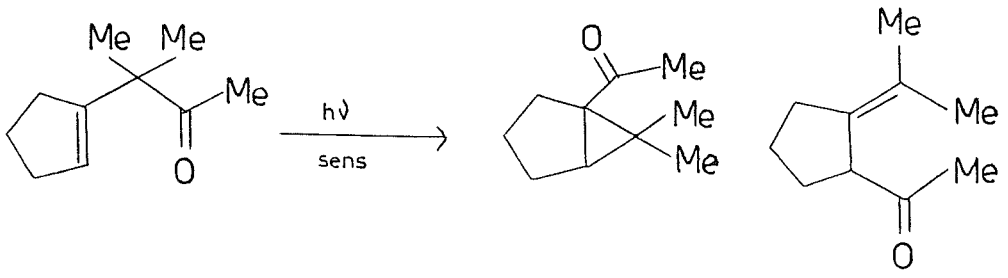
(18) (19) (20)

The oxa-di-π-methane rearrangement (1,2-acyl shift) is sensitive to minor structural changes. The cyclopentene



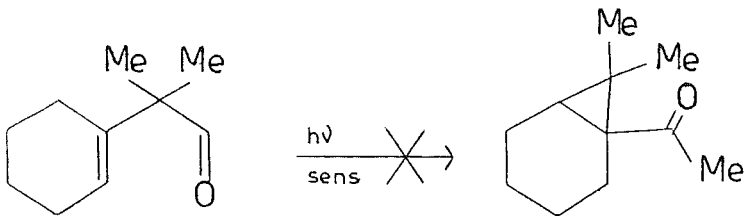
(21) (22)

system(21) undergoes sensitised irradiation to give the expected product(22) whereas the dimethyl analogue(23) gives the product of a 1,3-acyl shift(24) as well. The cyclohexene, cycloheptene and cyclooctene analogues are insensitive to



(23) (24)

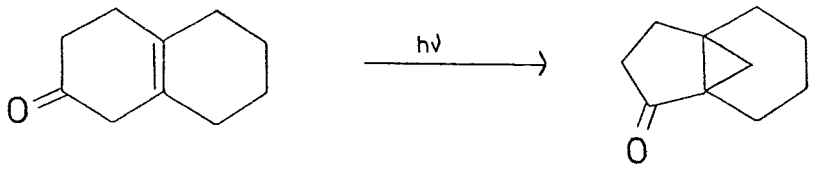
acetone-sensitised irradiation(Scheme 3) and Cookson and Rogers[15] postulated that this is due to preferential loss



Scheme 3

of triplet energy by ring twisting or possibly involvement of a different inactive lowest triplet state.

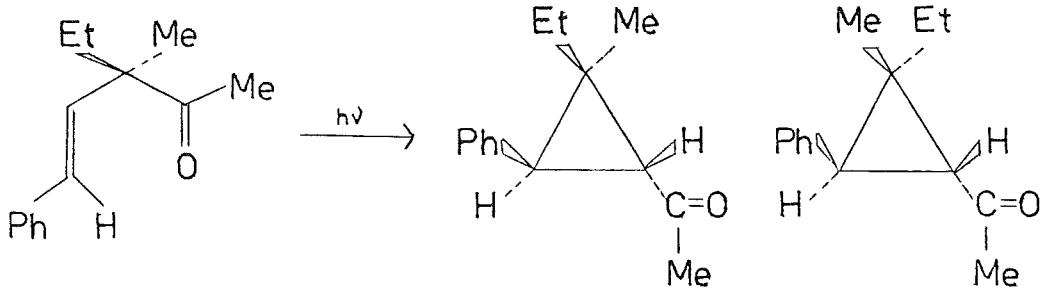
Although triplet sensitisation is generally required to observe the oxa-di-π-methane rearrangement, exceptions have been observed. For example, 3,4,5,6,7,8-hexahydronaphthalen-2-(1H)-one(25) forms the tricyclic ketone(26) on direct irradiation[16].



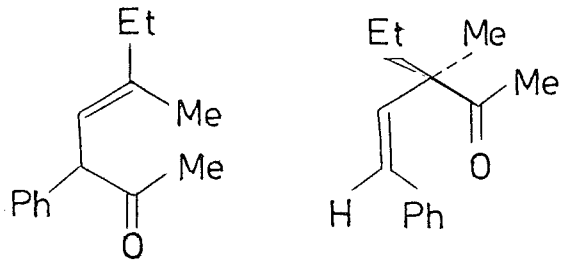
(25) (26)

The sensitised reactions of this compound yield no isolable products.

The oxa-di-π-methane rearrangement could follow a stepwise or a concerted mechanism. Sensitised irradiation of the optically active β,γ-unsaturated ketone(27)[17] gave, as well as other minor products(28,29), cyclopropane products (30,31) which were not more than 10% optically active.



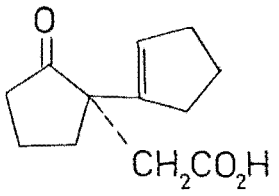
(27) (30) (31)



(28) (29)

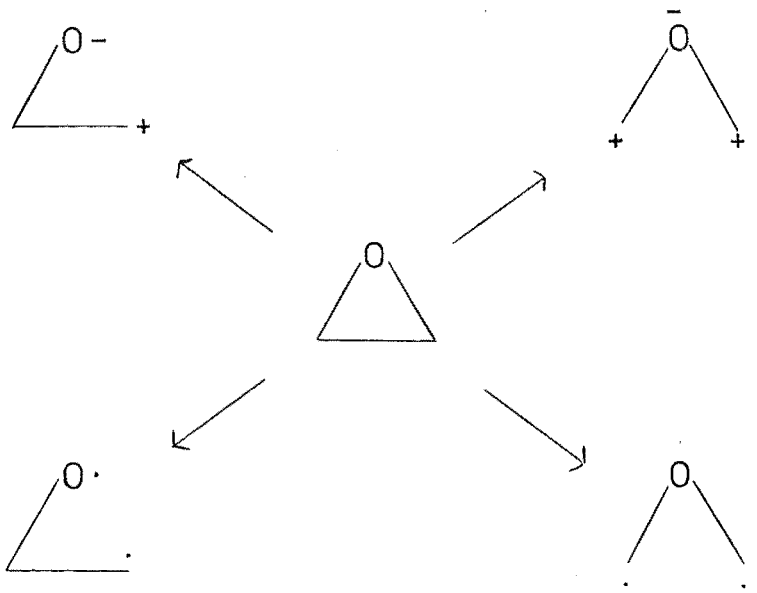
For concerted orbital symmetry-allowed mechanisms to produce nearly racemic products, the triplet of the *cis*-enone must follow one pathway and the triplet of the *trans*-enone the other, i.e.$[\pi_s^2 + \sigma_s^2]$ and $[\pi_a^2 + \sigma_a^2]$ respectively. This is unlikely and the oxa-di-π-methane rearrangement is generally regarded as occurring by a stepwise mechanism with at least

one achiral intermediate. However, the unsaturated ketone(32) rearranges with 90% inversion at the methane carbon.



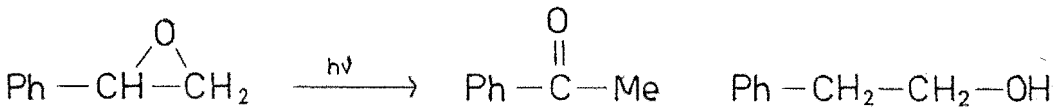
(32)

The photochemistry of epoxides has not received a great deal of attention to date. The strain energy of an epoxide provides a powerful thermodynamic driving force in any reaction. Photochemical excitation can induce ring cleavage if light of a suitable wavelength is used. The absorption spectrum of an epoxide can be shifted to the more accessible photochemical region by conjugation with unsaturated groups. Cleavage of the rings may involve zwitterionic or diradical intermediates(Scheme 4) and these intermediates give rise to (a) photofragmentation, (b) rearrangements and (c) reclosure of the ring.

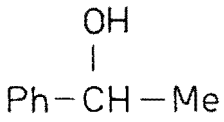


Scheme 4

Early studies[18] on ultra-violet light-initiated free-radical reactions of simple epoxides showed that both carbon-oxygen bonds in an unsymmetrical epoxide undergo homolytic cleavage to give alcohols and ketones. The photolysis of propylene oxide(33) gives acetone(34), 2-propanol(35), propanal(36), 1-propanol(37) and 2,5-hexanedione(38) and the following sequence(Scheme 5) was proposed to rationalise the products formed. Other mechanisms are possible for the formation of these products although rearrangement of (39) directly to acetone(34) and (40) to propanal(36) were neglected since 1,2-hydrogen atom shifts in diradical systems are considered to be very rare[19]. Styrene oxide(41) undergoes both C1-O and C2-O bond cleavage on photolysis[18]. Irradiation (2537Å) at 15°C for 72 hr however gave only a 0.3% conversion to acetophenone (42), 2-phenylethanol(43) and 1-phenylethanol(44).



(41) (42) (43)



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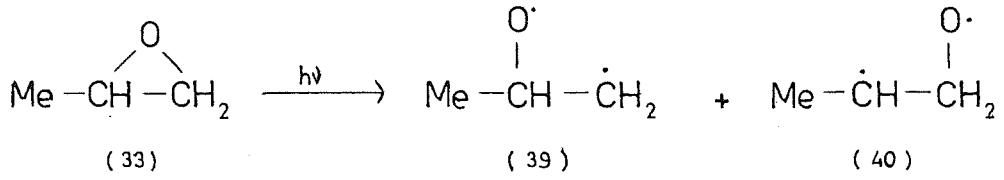
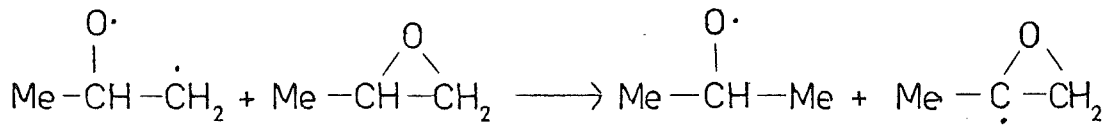
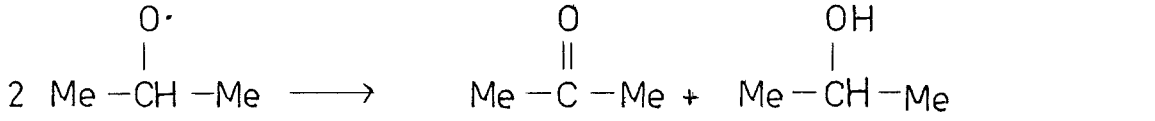
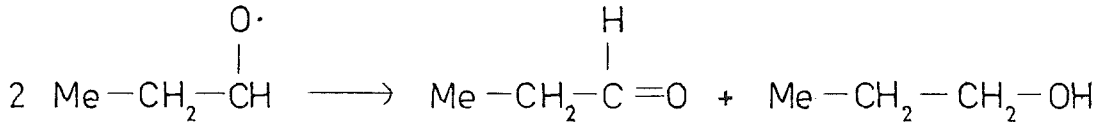


(33) (39) (40)





(34) (35)



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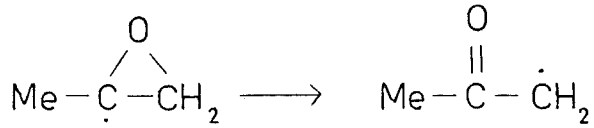

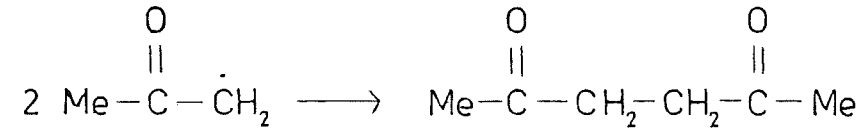

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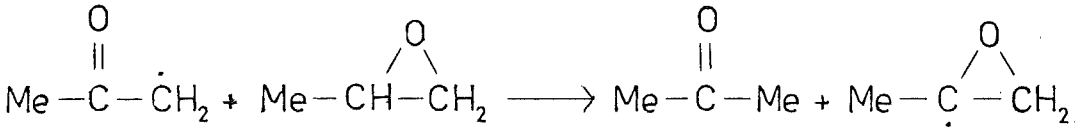
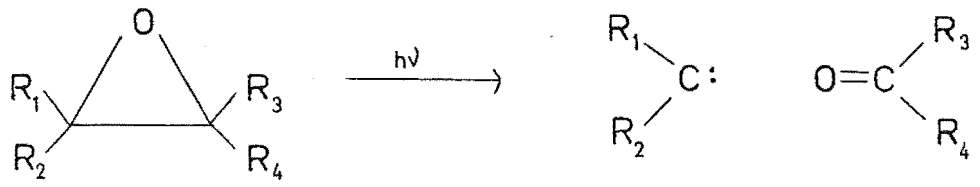


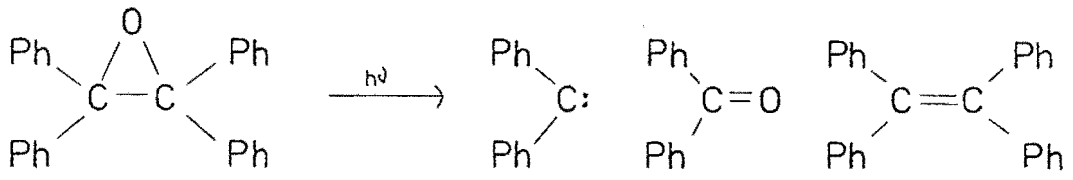
Scheme 5

Griffin[20] and his co-workers have shown that irradiation of phenyloxiranes generates unstable aryl carbenes in addition to aldehydes and/or ketones(Scheme 6). Continuous



Scheme 6

irradiation at -196°C of tetraphenyloxirane(45) produces a coloured species which can be bleached either by warming the sample above -180°C or by irradiation with visible light. Two discrete one-photon processes are thought to be involved. The first process involves the formation of the coloured intermediate, the second, recyclisation to the oxirane or fragmentation to carbene and ketone. The coloured intermediate was implicated in the fragmentation process by the observed bleaching of colour on irradiation with visible light and simultaneous production of the original oxirane(45) along with benzophenone(46), tetraphenylethylene(47) and diphenylmethylene(48).

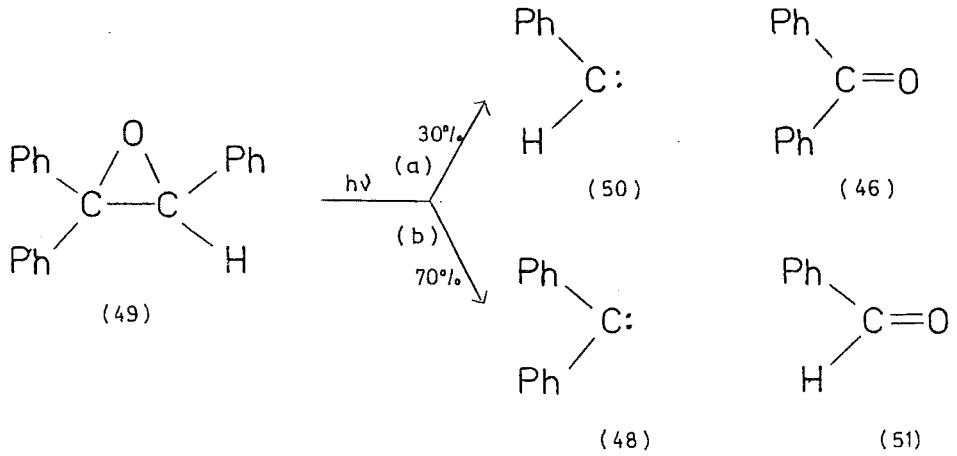


(45) (48) (46) (47)

Fragmentation of triphenyloxirane(49) on irradiation at -196°C occurs from the coloured intermediate in two ways:

(a) to give benzophenone(46) and phenylmethylene(50) and

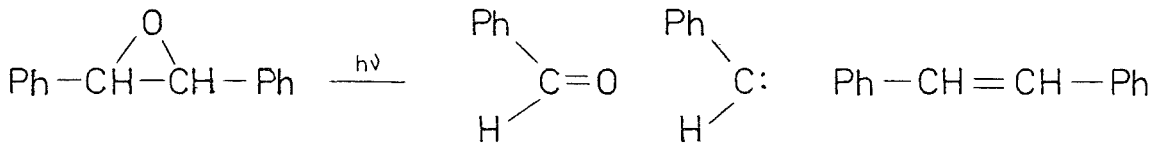
(b) to give benzaldehyde(51) and diphenylmethylene(48).



(49) (50) (46) (48) (51)

Triphenylethylene is also formed.

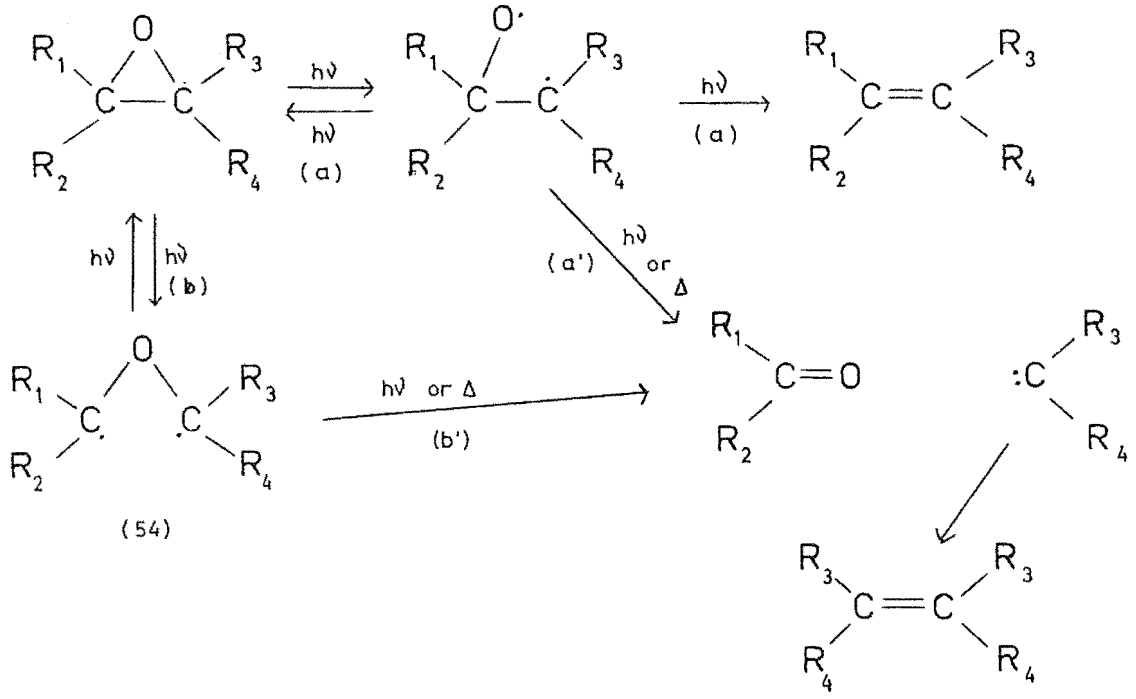
Irradiation of *trans*- or *cis*-2,3-diphenyloxirane(52) yields benzaldehyde(51), phenylmethylene(50) and the *trans*- or *cis*-stilbenes (53) respectively. The stilbene(53) is a primary



(52) (51) (50) (53)

photoproduct and is not formed by dimerisation of the carbene, phenylmethylene(50). It has been suggested that the solvent glass (at -196°C) is sufficiently rigid that bimolecular reactions do not occur.

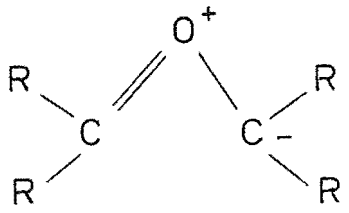
Irradiation of phenyloxirane(41) at -196°C does not form an observable coloured intermediate and labelling studies have shown that homolysis of the CH_2-O bond does not occur. The mechanism depicted in Scheme 7 is consistent with the experimental results obtained and while it is possible to



Scheme 7

explain all the products in terms of pathway (a), the diradical(54) may be involved.

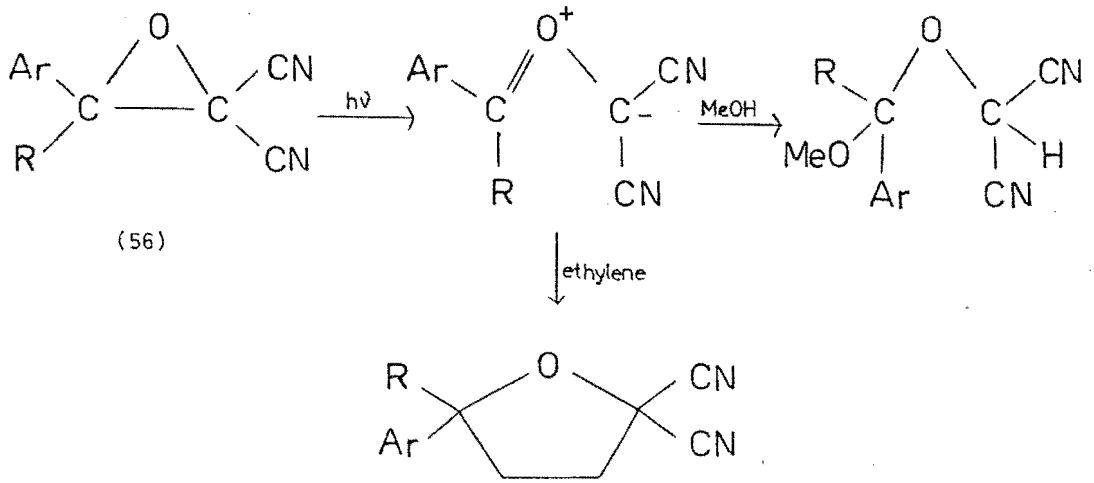
The coloured intermediates have been identified as carbonyl ylides(55)[21]. Their photochemical interconversion



(55)

with oxiranes is an allowed electrocyclic process. Direct evidence for the intermediacy of carbonyl ylides(55) has been obtained by investigation of the photochemistry of a series of dicyanooxiranes(56)[22-26]. Photofragmentation of oxiranes is suppressed in the absence of vicinal diaryl substitution and the carbonyl ylides formed on irradition of dicyanooxiranes have been intercepted by protic solvents such as methanol with

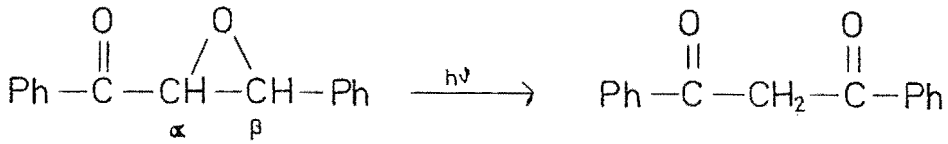
formation of ketals and acetals and by cycloaddition to dipolarphiles such as ethylene(Scheme 8).



(56)

Scheme 8

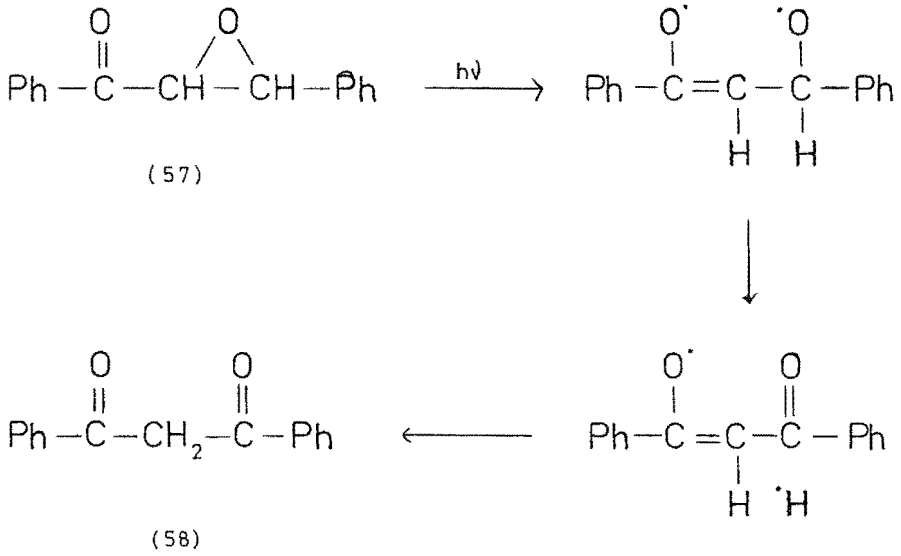
The effect of a second functional group proximate to an epoxide ring has been studied as early as 1918 for chalcone oxide(57) which rearranges to a 1,3-diketone(58)[27]. In general, the photolysis of α,β-epoxyketones follows a two step mechanism: C_α-O bond cleavage followed by a 1,2-shift



(57) (58)

of a β-substituent to the α-position. The driving force of the rearrangement has been attributed to the tendency of the n-π* excited state to eliminate α substituents as odd-electron or anionic species. The observed C_α-O bond cleavage is notably different to the preferred C_β-O cleavage on thermal or acid treatment. The mechanism of formation of the

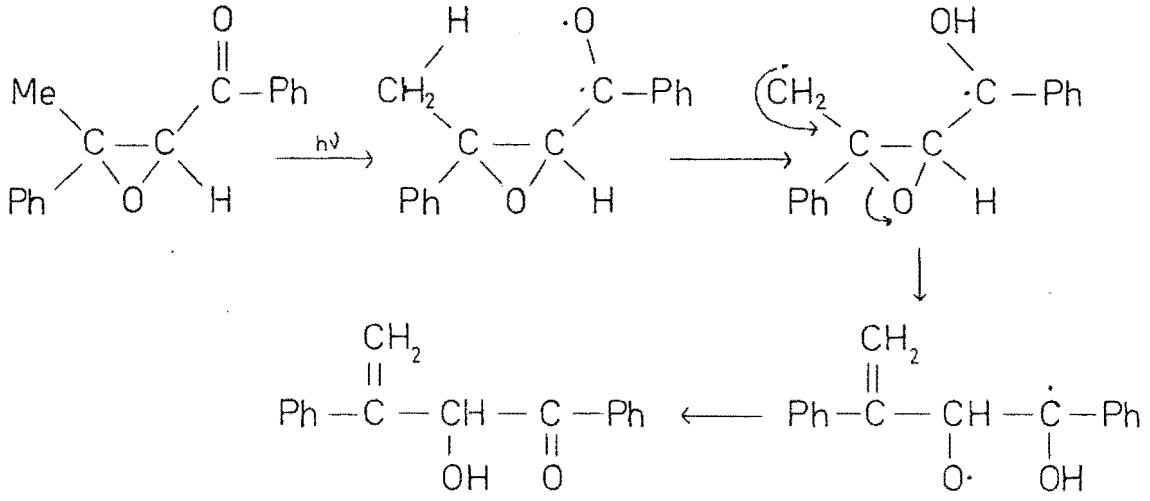
1,3-diketone(58) is depicted in Scheme 9. The 1,2-shift may be an intermolecular transfer or an intramolecular transfer inside a solvent cage[27]. Alternatively, the



Scheme 9

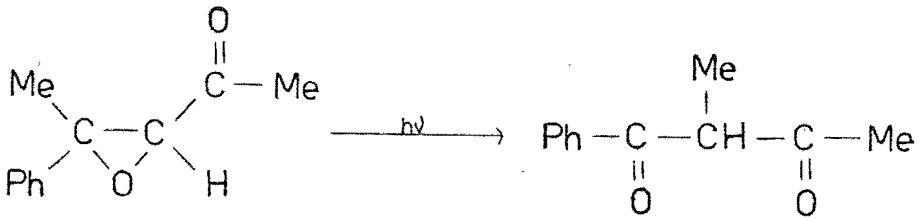
reaction may proceed by a concerted migration of hydrogen with C-O bond cleavage.

The presence of a γ-hydrogen in the proximity of the benzoyl moiety enables hydrogen abstraction to compete with migration with subsequent formation of an unsaturated ketol (Scheme 10)[28]. The reaction is sensitive to small



Scheme 10

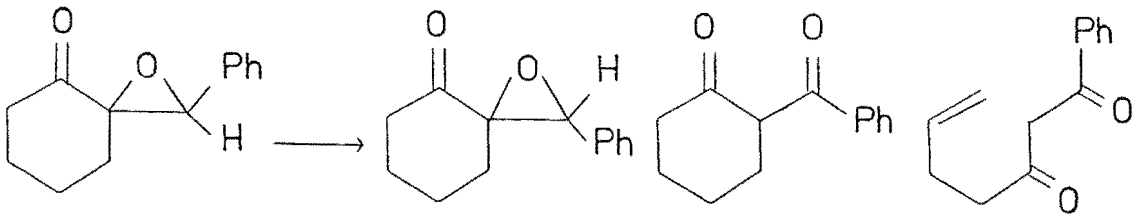
changes in epoxyketone structure. For example, (59) gives the diketone(60) on irradiation. Greater electron



(59) (60)

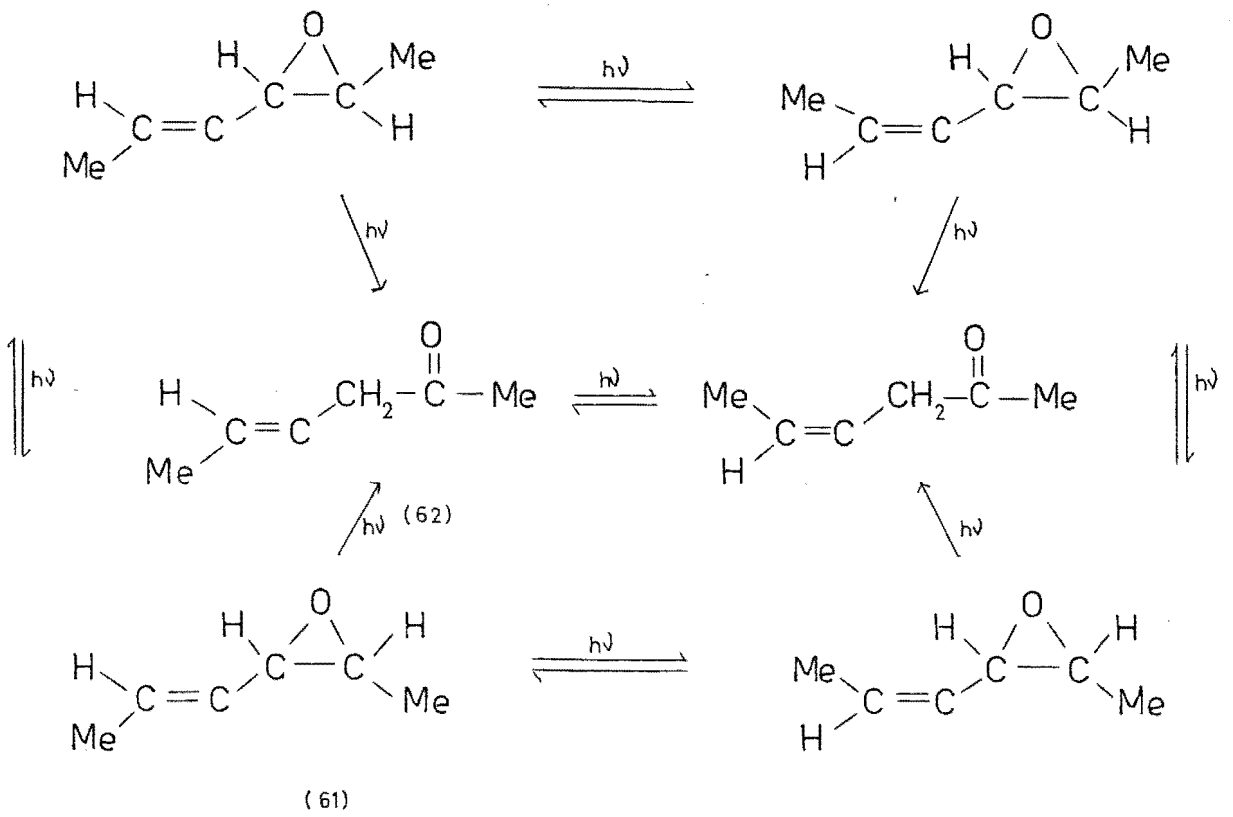
delocalisation in the alkyl substituted carbonyl group may favour β-elimination. From the n-π* excited state, groups attached to the carbon adjacent to an excited carbonyl group could be expelled heterolytically or homolytically. The preference for methyl migration over phenyl migration is rationalised by homolytic expulsion[28].

α,β-Epoxyketones have also been observed to undergo isomerisation at the epoxide carbons in a process involving C-C bond cleavage (Scheme 11)[29]. 4,5-Epoxyhex-2-ene(61)



Scheme 11

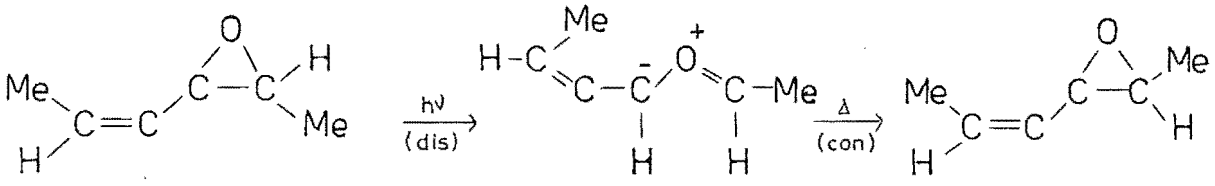
undergoes acetone sensitised geometric isomerisation of both the alkene and the epoxide moieties as well as epoxide ring opening and formation of the β,γ-unsaturated ketones(62) (Scheme 12)[30]. It is suggested that epimerisation of the epoxide moiety occurs by C-C bond cleavage with formation of an intermediate carbon ylide(63). Photochemically allowed



(61)

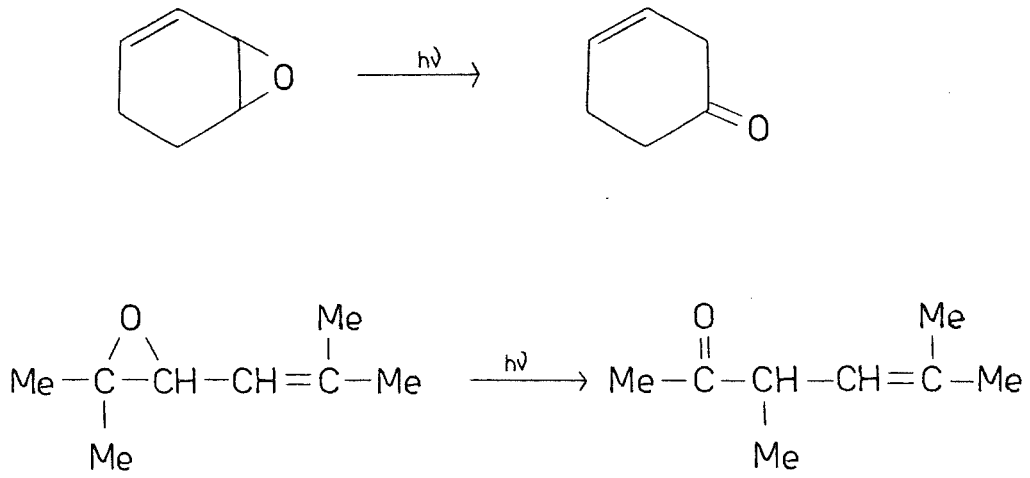
Scheme 12

disrotatory opening of the epoxide ring followed by thermally allowed conrotatory ring closure would effect this isomerisation; however, the presence of a normally efficient ylide trapping agent failed to trap the ylide (63).



(61) (63) (61)

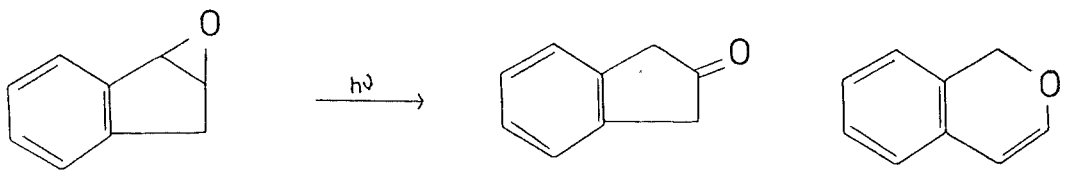
Irradiation of acetone solutions of 3,4-epoxyolefins results in the formation of β,γ-unsaturated ketones (Scheme 13)[31]. The ketones are formed by C-O bond cleavage and



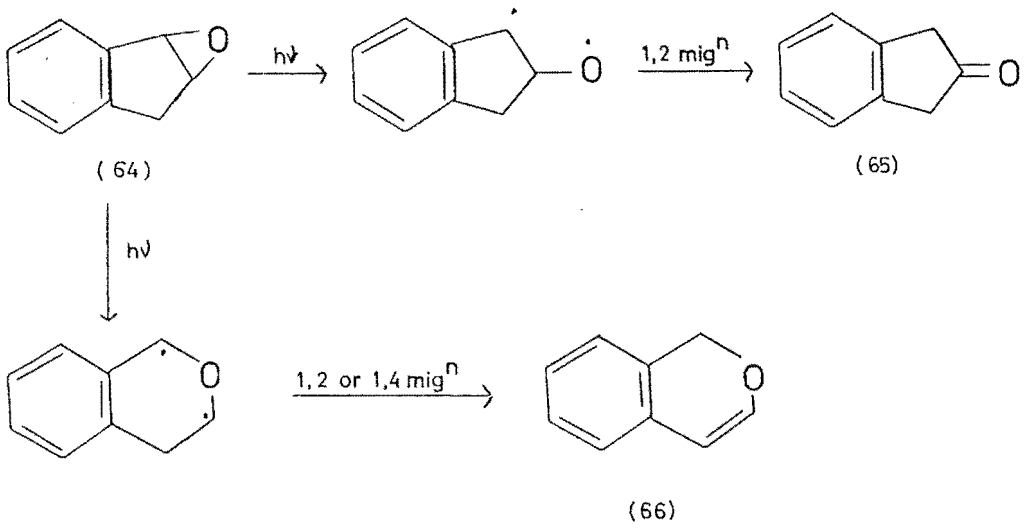
Scheme 13

1,2-hydrogen or alkyl migrations. Paulson[31] observed that 1,2-hydrogen shifts rarely occur and suggested that the reaction is symmetry forbidden[32]. He proposed that 1,2-radical migration might become favourable since the energy gained in the formation of the carbonyl group may overcome the non-allowed nature of the reaction.

The photolytic rearrangement of indene oxide(64)[33] to indan-2-one(65) is analogous to the above α,β-unsaturated epoxide systems. Isolation of isochromene(66) from the reaction mixture implies that epoxide C-C bond cleavage occurs followed by 1,2- or 1,4-migration(Scheme 14).

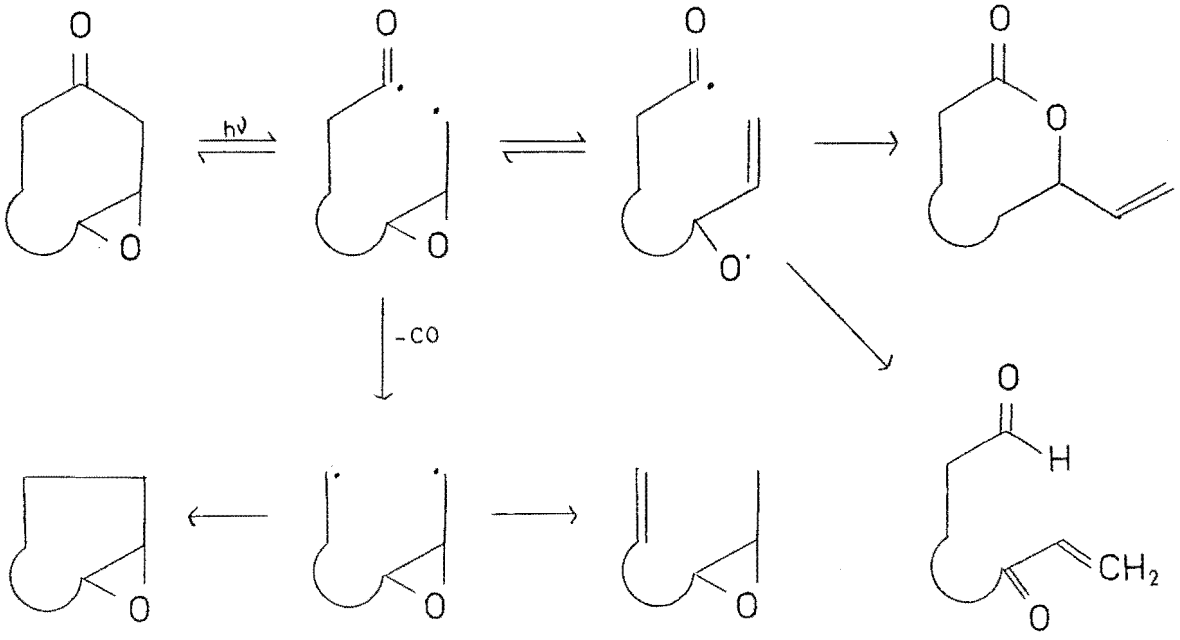


(64) (65) (66)



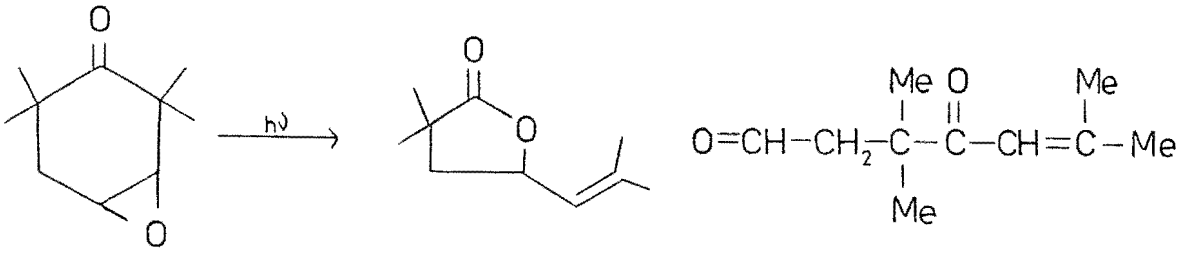
Scheme 14

Although the photochemical reactions of α,β-epoxyketones have received considerable attention, only a few reports have appeared concerning the photochemistry of β,γ-epoxyketones[34-37]. Murray and his co-workers[38] have reported a general scheme which summarises the photochemistry of the β,γ-epoxy cyclic ketones that they studied(Scheme 15). The initial step



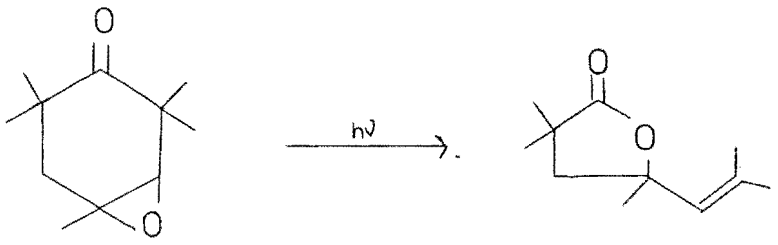
Scheme 15

involves Norrish type I bond cleavage and formation of the diradical. Ring opening of the epoxide gives an acyl alkoxy diradical. In the absence of specific constraints or substituent effects, competitive ring closure to form a lactone and hydrogen transfer to give an aldehyde occurs. If one reaction is inhibited, the other dominates. For example, 2,2,6,6-tetramethyl-3,4-epoxycyclohexanone(67) has no unusual molecular constraints and on irradiation forms



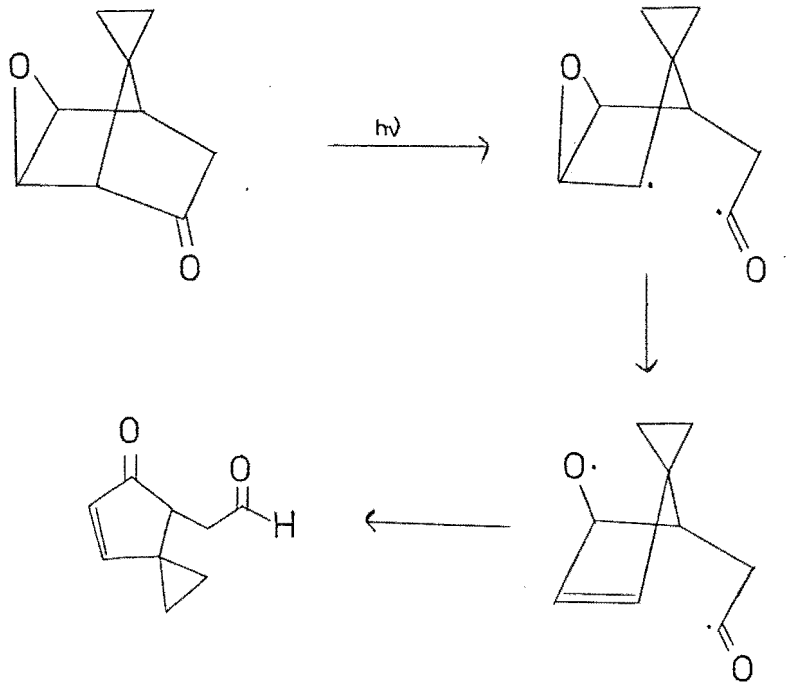
(67) (68) (69)

both lactone and aldehyde products(68, 69). Aldehyde formation is prevented by a C4-methyl substituent and for this substrate(70) only lactone(71) is formed. Geometric



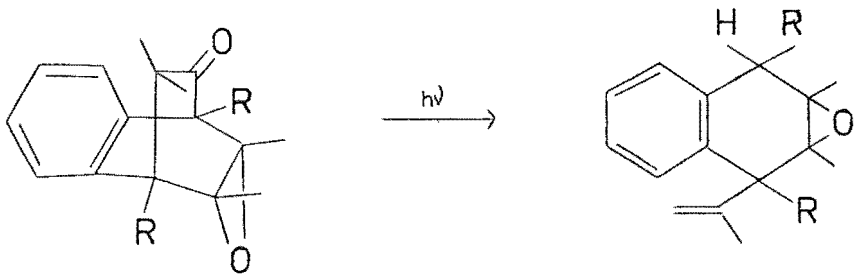
(70) (71)

constraints may inhibit lactone formation as depicted in Scheme 16. If the formation of both the lactone and



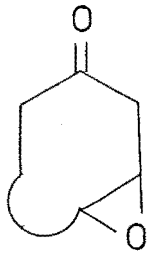
Scheme 16

aldehyde is prevented, decarbonylation occurs to give the diradical which undergoes disproportionation and/or ring closure(Scheme 17). The general scheme outlined above

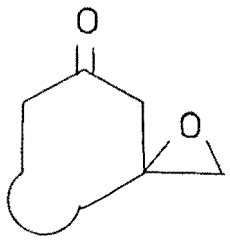


Scheme 17

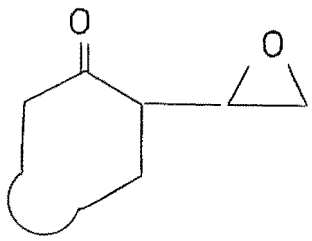
is found to hold, with few exceptions[39], for the three types of β,γ-epoxy cyclic ketone systems (72), (73) and (74) depicted below.



(72)

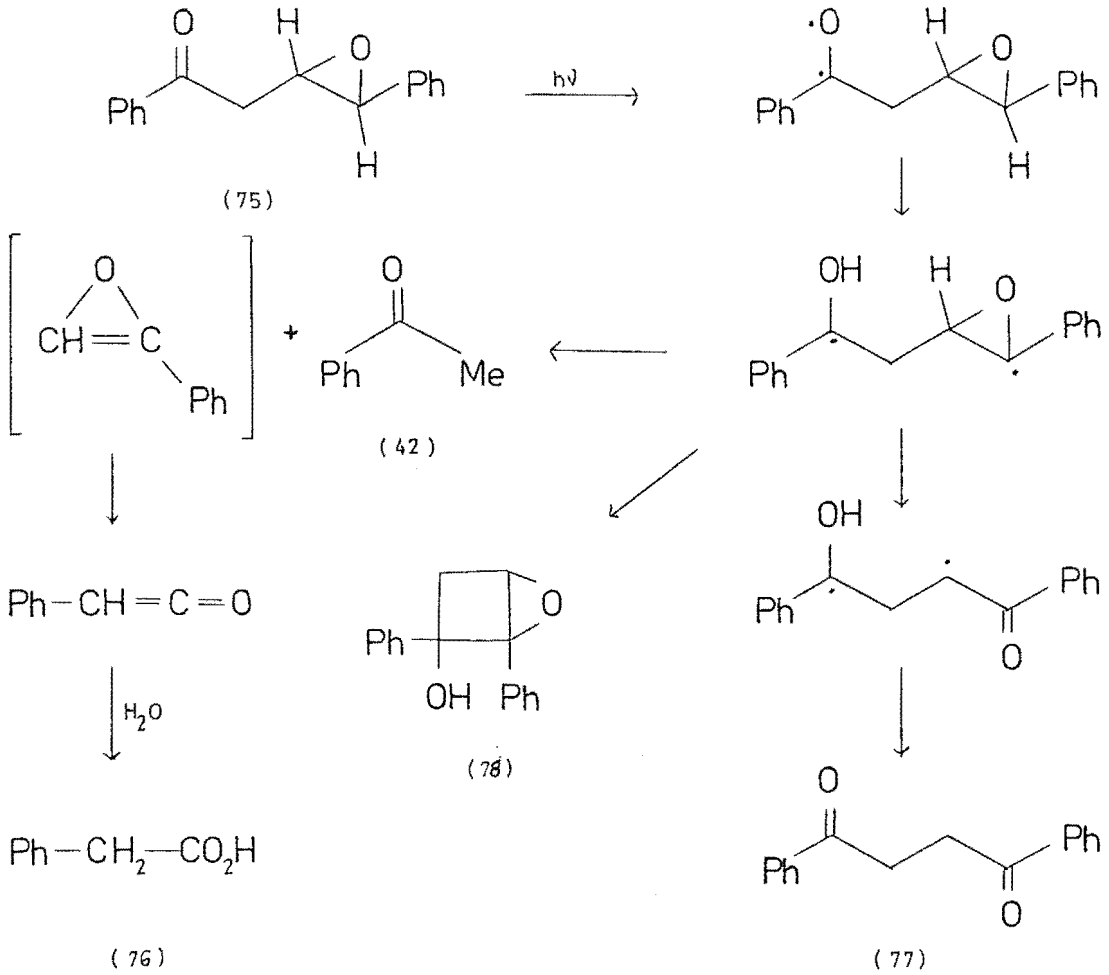


(73)



(74)

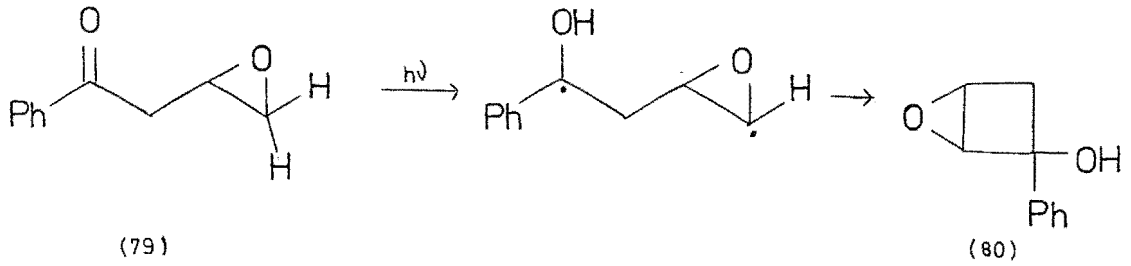
Only two groups have studied the photolysis of acyclic β,γ-epoxyketones. Padwa *et al*[40] reported the photolysis of 1,4-diphenyl-3,4-epoxybutanone(75). The products isolated were acetophenone(42), phenylacetic acid(76), dibenzoylethane (77) and 1,2-diphenyl-2,3-epoxybutanol(78) and the mechanism depicted in Scheme 18 was proposed to explain the formation



Scheme 18

of these products.

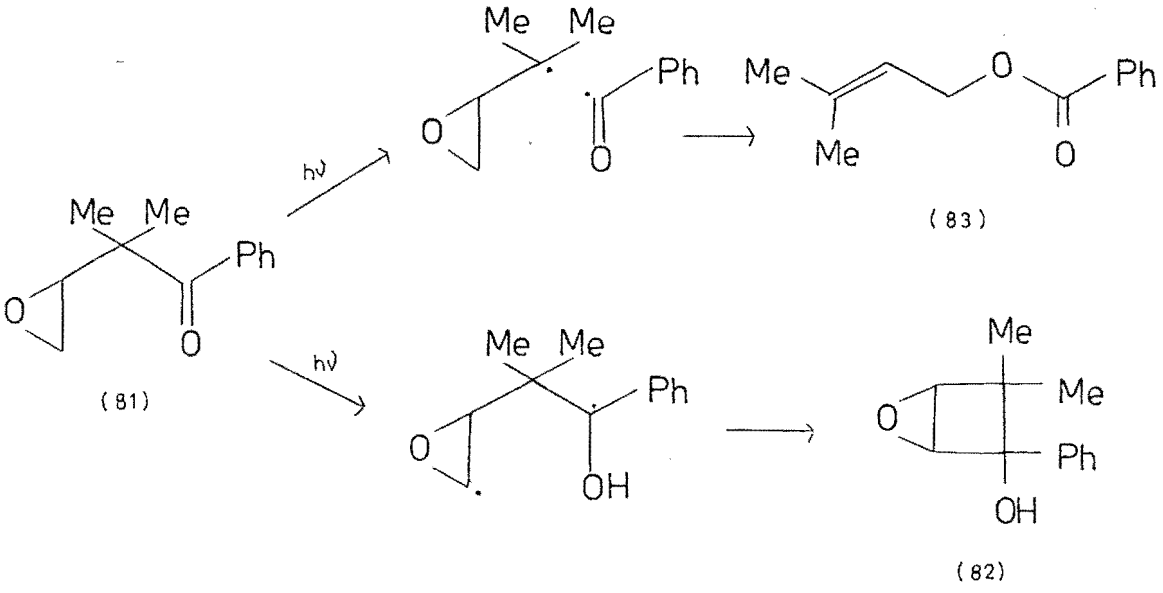
Coxon and Hii[41] found that the photolysis of 3,4-epoxy-1-phenylbutan-1-one(79) gave two isomers of 2,3-epoxy-1-phenylcyclobutanol(80) by abstraction of a



(79) (80)

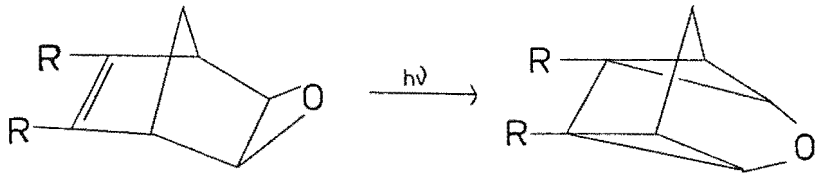
Scheme 19

γ-hydrogen by the excited carbonyl moiety followed by ring closure of the 1,4-diradical(Scheme 19). Acetophenone(42) was detected only in trace amounts. Photolysis of 2,2-dimethyl-3,4-epoxy-1-phenylbutan-1-one(81) resulted in the formation of very little cyclobutanol product(82). The major isomer isolated was 3-methylbut-2-en-1-yl benzoate(83) which is envisaged as arising from α-cleavage, facilitated by the presence of the *gem*-dimethyl group, and bond formation between the oxygen of the oxyalkyl radical and the benzoyl radical(Scheme 20).



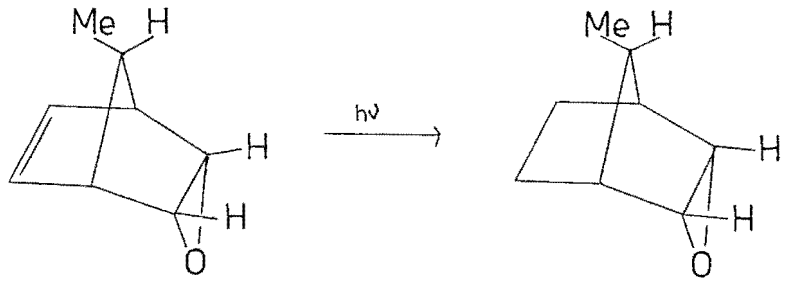
Scheme 20

Although the photolysis of molecules which contain alkene, epoxide and ketone moieties has been studied[42-44], only two reports of the photolysis of the β,γ-unsaturated epoxide system have been found. Prinzbach and Klaus[45] showed that valence isomerisation between an alkene bond and an oxirane ring could be achieved photochemically by irradiation of the substituted *exo*-epoxynorbornene(84) in CH_3CN. Padwa



(84)

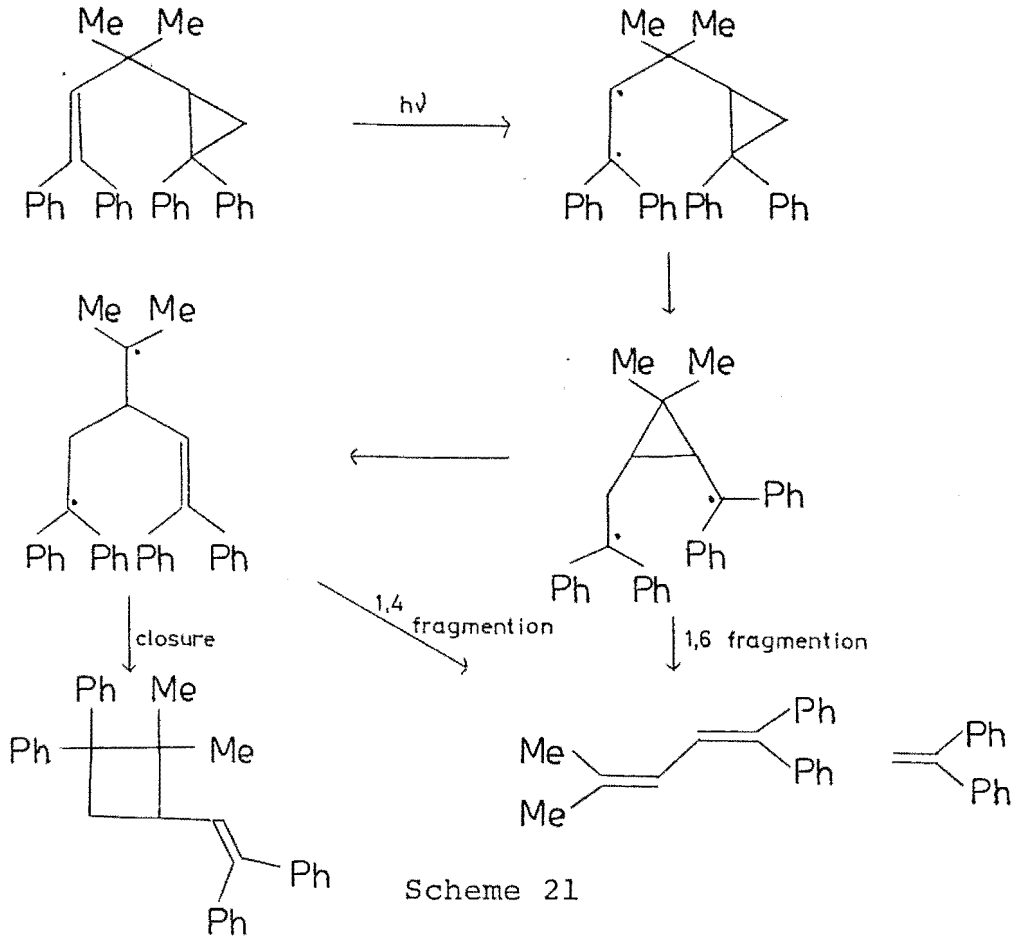
and Koehn[46] found that the *endo*-norbornene epoxide(85) undergoes reduction in acetone. It was proposed that the triplet



(85)

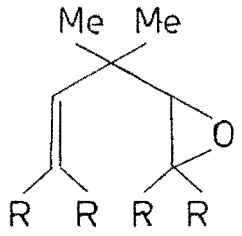
state of the norbornene epoxide is sufficiently long lived to participate in an intermolecular hydrogen atom abstraction.

Because of the general nature of the di-π-methane rearrangement in 1,4-dienes, it was of interest to ascertain if the counterpart process in which one π bond is replaced by a three-membered ring would occur. Replacement of the vinyl bond by a cyclopropane ring gives the β,γ-unsaturated cyclopropane system. Zimmerman[47] has studied the photochemistry of such a system which was found to react via a mechanism parallel to the di-π-methane rearrangement(Scheme 21).

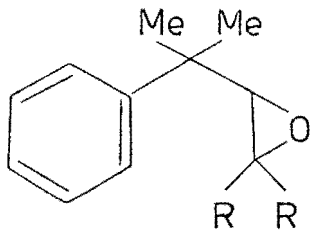


Scheme 21

The purpose of the present study was to investigate the replacement of a vinyl bond in a 1,4-diene by an epoxide ring(86) and an aryl group(87) to see if a

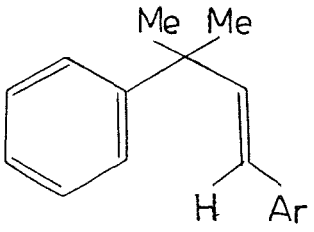


(86)

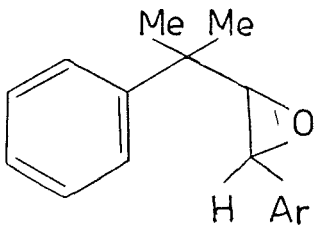


(87)

rearrangement analogous to the di-π-methane rearrangement could be observed, or in fact to see the effect of these different chromophores on each other in the photochemical reaction. In addition, the photolysis of the *trans*-1-aryl-3-methyl-3-phenylbut-1-enes(88), precursors to the epoxides(89) have been studied to determine the effect of substituents on the course of the reaction.



(88) a-g



(89) a-f

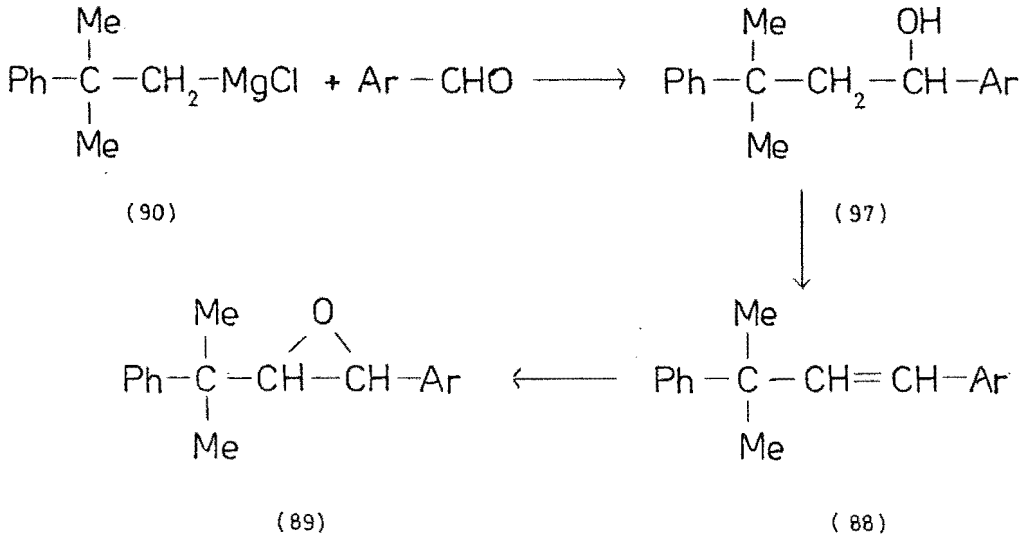
Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl
(f) 3',4'-Ph-Cl
(g) p-Ph-CN

Preparation of *trans*-1-aryl-3-methyl-3-phenylbut-1-enes(88) and *trans*-1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes(89)

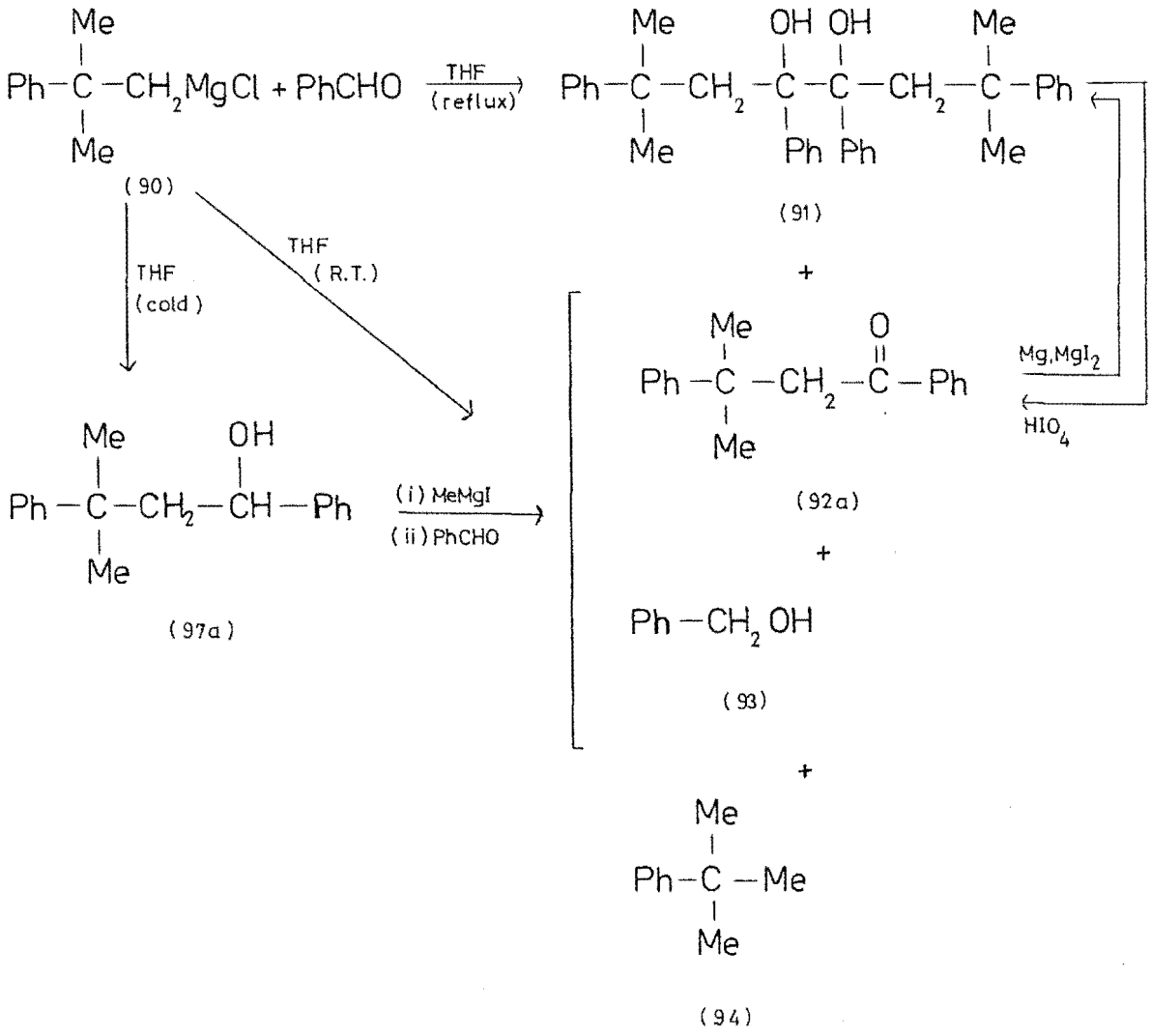
To prepare the required epoxides(89a-f), it was planned to use a simple procedure involving a Grignard reaction between 2-methyl-2-phenylprop-1-ylmagnesium chloride(90) and the appropriately substituted benzaldehydes followed by dehydration and epoxidation(Scheme 22). The reaction of the Grignard reagent(90) with benzaldehyde has been previously reported[48]. In this present investigation, the Grignard reagent(90) was slow to form even in refluxing ether, and tetrahydrofuran was substituted. This reaction was found to be particularly sensitive to the reaction conditions both during and after the addition of benzaldehyde (Scheme 23).

Addition of benzaldehyde to the Grignard reagent(90) at room temperature followed by heating under reflux gave *dl*-and *meso*-2,7-dimethyl-2,4,5,7-tetraphenyloctane-4,5-diol (91a,b) (31%), 1,3-diphenyl-3-methylbutan-1-one(92a) (17%), benzyl alcohol(93) (23%) and 2-methyl-2-phenylpropane(94) (16%). On standing, the crude reaction product oil deposited crystals which were recrystallised from chloroform to give two distinct crystalline forms,long needles(91a) and irregular hexagonal plates(91b) which were separated manually.

The ^{1}Hn.m.r. spectrum of the needle-like crystals(91a) showed the presence of two methyl groups by single peaks at δ_H0.75 and δ_H 1.00. An AB quartet (δ_H2.75, 1.68, J 15Hz) indicated non-equivalent methylene protons and a single peak at δ_H2.02, removed after shaking with D_2O, confirmed the presence of the hydroxyl proton, also observed in the i.r. spectrum with ν 3590 cm^{-1}.



Scheme 22



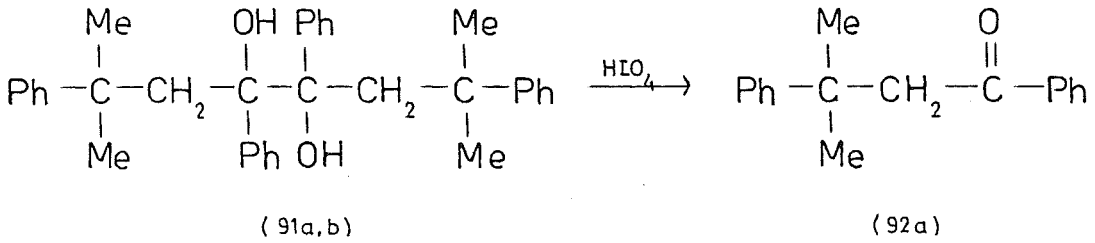
Scheme 23

The signal at δ_H 7.20 showed the presence of aromatic protons. The ^{13}Cn.m.r. and sford spectra of these crystals(91a) confirmed the presence of two methyl groups (δ_C27.4, 34.4), one methylene carbon (δ_C45.7) and two aromatic rings which differed only in the chemical shift of the two *ipso* carbons (δ_C142.2, 150.0, 125.7, 128.4, 126.5). The ^{13}Cn.m.r. spectrum further showed the presence of quaternary carbons with signals at δ37.5 and δ81.4. The absence of any other signals indicated the structure to be a symmetrical diol(91). The parent ion in the mass spectrum was not observed, the molecule fragmenting to give for the largest observed fragment a peak at m/z 239.1430.

The ^{1}Hn.m.r. spectrum of the plate-like crystals(91b) showed two singlet peaks (δ_H0.75, 0.90) indicating the presence of two methyl groups. A signal at δ_H2.22 was due to methylene protons in equivalent environments and the peak at δ_H1.39 was removed after shaking the sample with D_2O. The relative integral of the singlet at δ_H6.95 showed that the compound contained ten aromatic protons. The ^{13}Cn.m.r. spectrum of (91b) was remarkably similar to the spectrum of (91a) except that the signals were offset by C.2 ppm. The spectrum confirmed the presence of the two methyl groups (δ_C26.6, 35.1) and the single methylene carbon (δ_C46.9). The two phenyl rings were represented by seven signals (δ_C149.1, 126.2, 128.3, 125.5, 144.6, 125.3, 128.3, 127.9). The sford spectrum showed that the signals at δ_C37.1 and δ_C81.5 were due to quaternary carbons. The mass spectrum did not show a parent peak for the diol(91b), the highest mass peak being m/z 239.1441.

For a mixture of the diols(91a,b) reaction with periodic acid resulted in a quantitative yield of

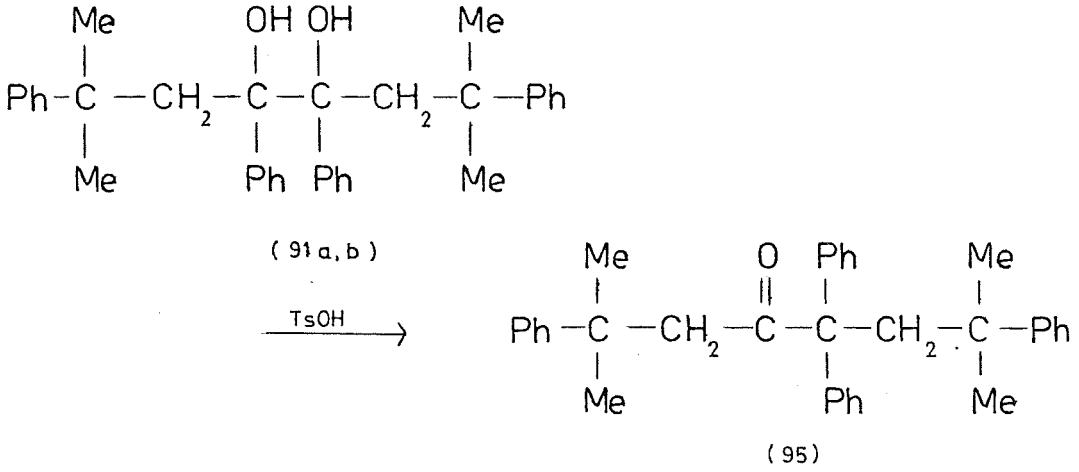
1,3-diphenyl-3-methyl-butan-1-one(92a)[49]. The i.r. spectrum



(91a,b) (92a)

ν_{max} 1670, 1690 cm^{-1} and the ultraviolet spectrum λ_{max} 211nm(ε6058), 238(7885) of the ketone(92a) confirmed the conjugation of the carbonyl group to a phenyl ring. The ^{1}Hn.m.r. spectrum showed the presence of two methyl groups as a singlet peak (δ_H1.50) and the methylene protons appeared as a singlet at δ_H3.27. The multiplet centered at δ_H7.50 (Wh/2 43Hz) was consistent with the presence of ten aromatic protons. The ^{13}Cn.m.r. spectrum showed the presence of the methyl carbon signal (δ_C29.1), a single methylene carbon peak (δ_C50.8), a carbonyl carbon signal (δ_C199.0), a quarternary carbon peak (δ_C37.5) and two phenyl rings as eight peaks (δ*ipso* 138.2, 148.8 ; δ*ortho* 128.3, 125.4 ; δ*meta* 128.0, 128.1 ; δ*para* 132.6, 125.7).

The dimeric nature of the diol(91) was firmly established by the observation that the mixed diols(91a,b) (*c*.1:1) underwent a pinacol-pinacolone rearrangement on reaction with *p*-toluenesulphonic acid to give a near-quantitative (97%) yield of 2,7-dimethyl-2,5,5,7-tetra-phenyloctan-4-one(95). The i.r. spectrum (ν_{max} 1715 cm^{-1}) showed that the ketone(95) carbonyl group was not conjugated with an aromatic group. The ^{1}Hn.m.r. spectrum of the ketone(95) showed two peaks (δ_H1.00, 1.30) for the four methyl groups, two peaks (δ_H2.70, 2.92) for the four methylene

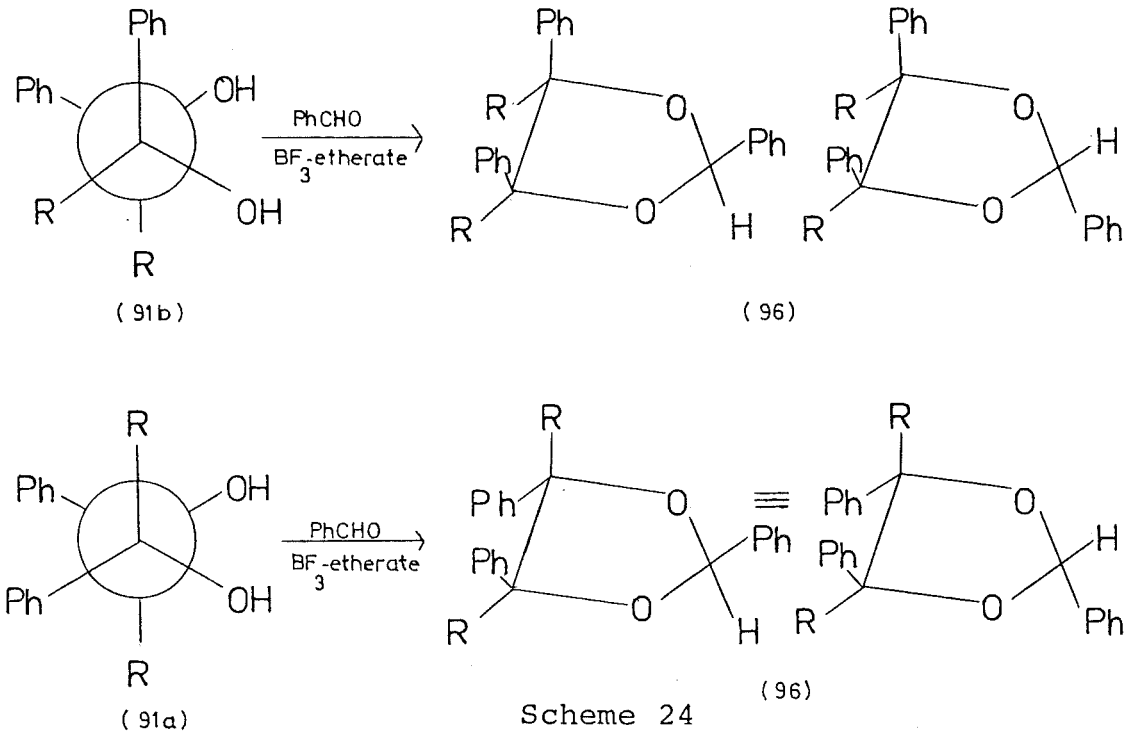


(91a,b) —TsOH→ (95)

protons and a multiplet centered at δ_H7.15 (Wh|2 22Hz) for the aromatic protons. In the ^{13}Cn.m.r. spectrum the methyl carbons appeared as two peaks (δ_C29.8, 28.5) and the carbonyl carbon signal appeared at δ_C202.9. The sford spectrum showed the presence of two methylene carbon signals (δ_C50.5, 49.6) and three quaternary carbon peaks (δ_C36.9, 37.9, 65.8). Three different phenyl groups were observed (*δipso* 141.2, 149.2, 150.3 ; *δortho* 125.2, 125.4, 130.2 ; *δmeta* 127.6, 127.7, 127.8 ; *δpara* 124.7, 126.6, 128.3) while the relative amplitude of the peaks showed that the signals of two of the phenyl rings overlapped.

To determine which crystalline form of the diol(91) was the *meso* isomer and which was the *dℓ* isomer, an attempt was made to prepare a dioxalane derivative(96). The *meso* isomer of the diol should react with benzaldehyde to give two spectroscopically different dioxalane derivatives whereas the *dℓ* isomer should form only one dioxalane(Scheme 24). Repeated attempts to form dioxalanes were unsuccessful probably due to the bulk of the substrate preventing ring closure.

An X-ray diffraction study was carried out on the plate-like crystals(91b). X-ray photographs unambiguously established the following crystal data for these crystals : m.p. 178-179°C; $C_{34}H_{38}O_2$, M = 478.7, orthorhombic, space group



Scheme 24

Pbca, a = 18.28, b = 21.14, c = 7.19Å, ν = 2777Å, D_m = 1.14 gcm^{-3} (by floatation), z = 4, D_c = 1.15 gcm^{-3}. Since there are eight general equivalent positions in this space group these dimeric units must lie about a crystallographic center of symmetry. Thus this isomer(91b) is *meso* and hence the needle-like crystals(91a), m.p. 152-154°C must be *dl*.

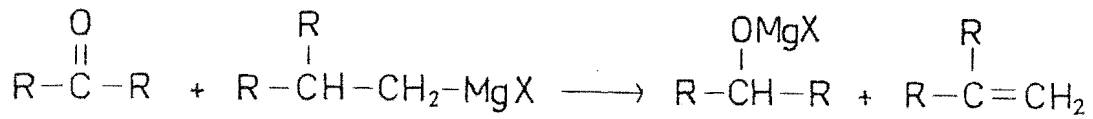
The remaining products formed in the reaction of benzaldehyde and 2-methyl-2-phenylpropylmagnesium chloride(90) were identified from their spectral data. The ketone, 1,3-diphenyl-3-methylbutan-1-one(92a) was identical to that obtained by periodic cleavage of the diol(91). Benzyl alcohol(93)[50] and 2-methyl-2-phenylpropane(94)[51] are both known compounds.

In a separate experiment the Grignard reagent(90) was cooled in ice before benzaldehyde was added. The reaction mixture was kept at room temperature overnight and the products isolated and identified as 1,3-diphenyl-3-methylbutan-1-one(92a) (46%), benzyl alcohol(93) (49%),

1,3-diphenyl-3-methylbutan-1-ol(97a) (3%) and 2-methyl-2-phenyl-propane(94) (2%).

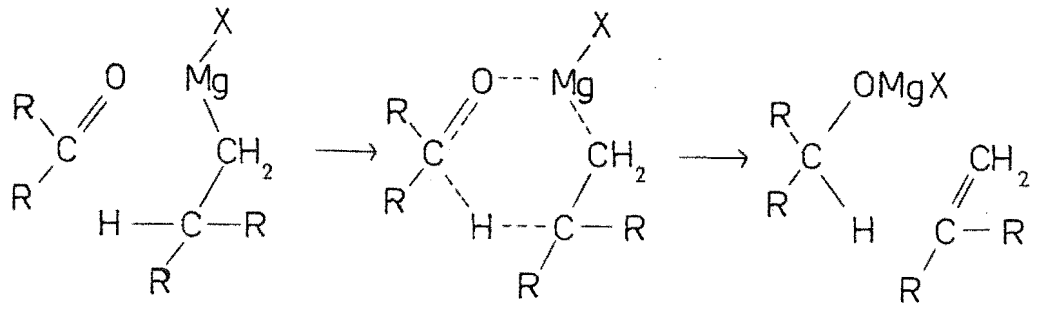
After repeated attempts varying the reaction conditions it was found that 1,3-diphenyl-3-methylbutan-1-ol(97a) could be obtained in high yield (>90%) by adding the aldehyde to the Grignard reagent(90) and keeping the reaction mixture at room temperature for 1hr. The presence of the hydroxyl in the product was shown from the infrared spectrum (ν_{max} 3450 cm^{-1}). The ^{1}Hn.m.r. spectrum showed the presence of two singlet methyl peaks (δ_H1.38, 1.42) and the hydroxyl proton as a singlet at δ_H1.55. The ten aromatic protons appeared as a narrow multiplet (Wh|2 2Hz) at δ_H7.26 and the methylene protons as a complex multiplet, centered at δ_H2.08, coupled with each other and the Cl proton. Hl appeared as a doublet of doublets (δ_H4.40) being coupled with the two methylene protons.

The formation of 1,3-diphenyl-3-methylbutan-1-one(92a) and benzyl alcohol(93) in the reaction of benzaldehyde and 2-methyl-2-phenylpropylmagnesium chloride(90) is not completely without precedence. Shankland and Gomberg[52] demonstrated in 1930 that aliphatic Grignard reagents can under certain conditions reduce aldehydes and ketones. They claimed that the Grignard reagent was itself oxidised to an unsaturated hydrocarbon and were able to isolate alkenes from such a reaction(Scheme 25). They further noted the need of a



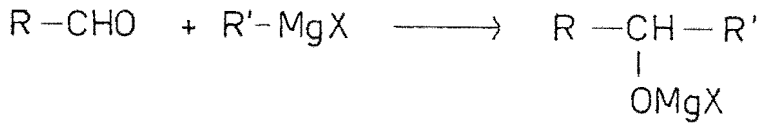
Scheme 25

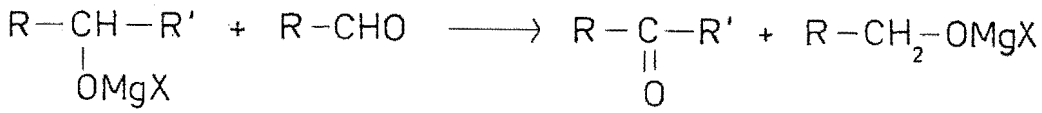
β-hydrogen atom before alkenes were formed. Miller *et al*[53] and Foley *et al*[54] argue that the reaction involves a six-membered transition state(Scheme 26).



Scheme 26

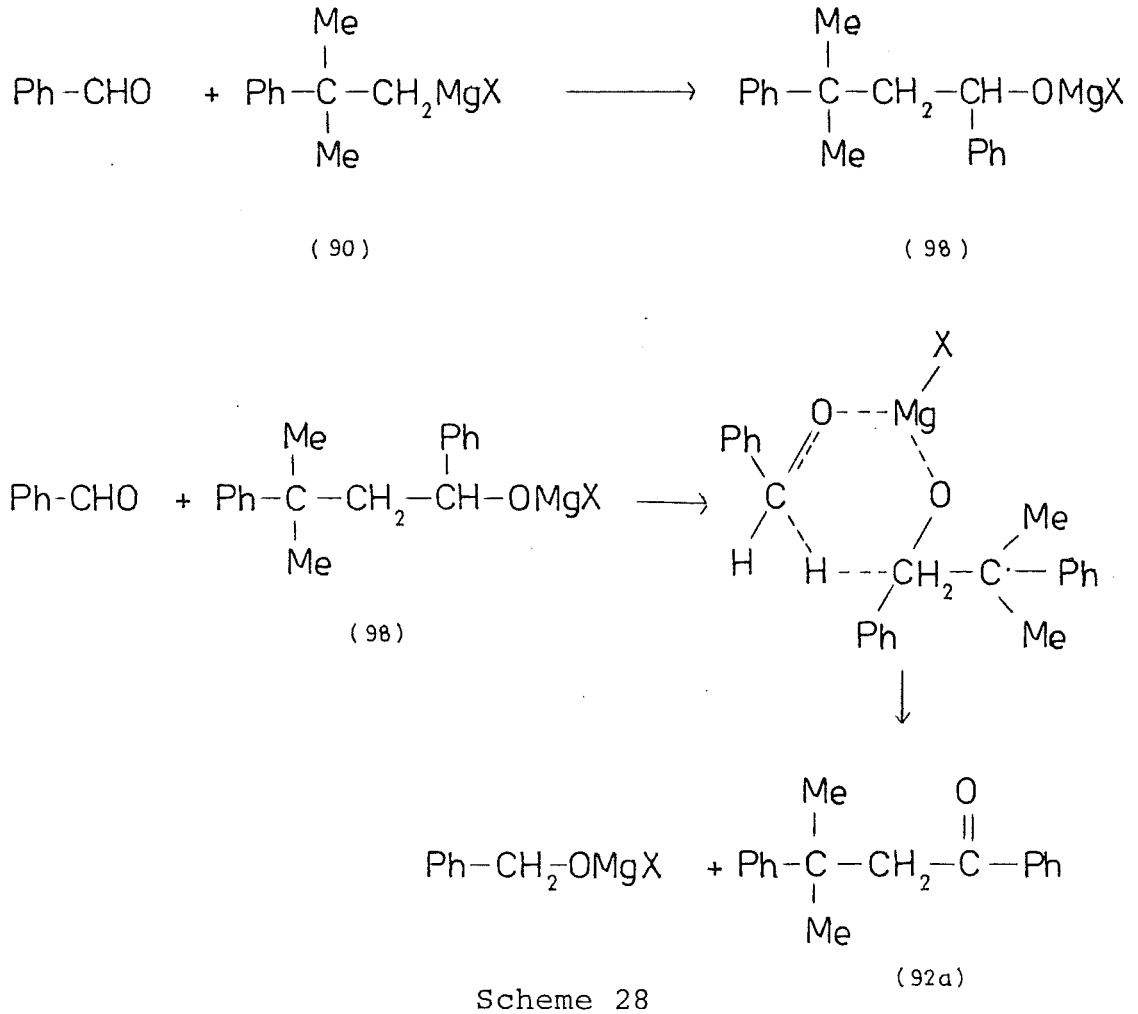
For a Grignard reaction in which the reagent does not have a β-hydrogen atom, reduction of a carbonyl can still occur. An initially formed ROMgX may be involved in the reduction(Scheme 27) and an analogous mechanism





Scheme 27

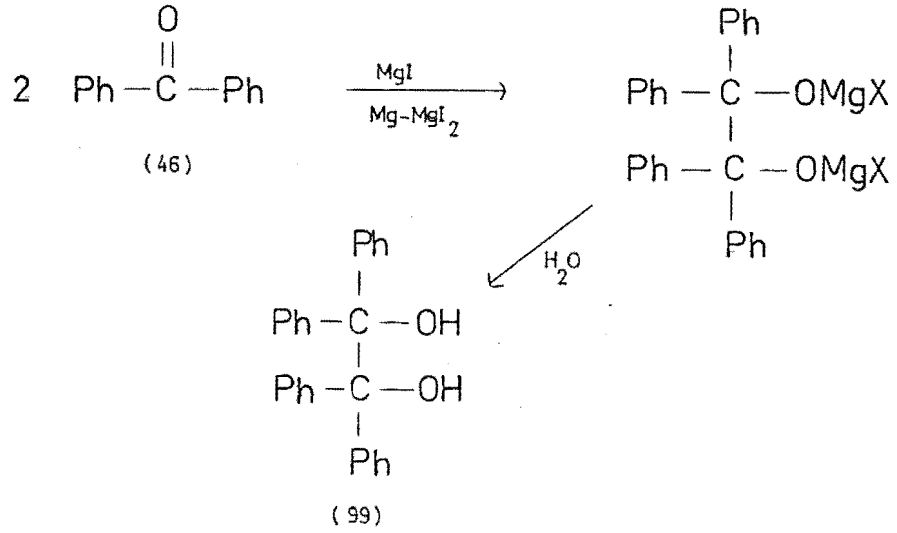
involving a six-membered transition state can be written for the reduction of the carbonyl with ROMgX. This is shown for the formation of the ketone, 1,3-diphenyl-3-methylbutan-1-one(92a) in the reaction of benzaldehyde and 2-methyl-2-phenylpropylmagnesium chloride(90) in Scheme 28. To demonstrate that this mechanism was



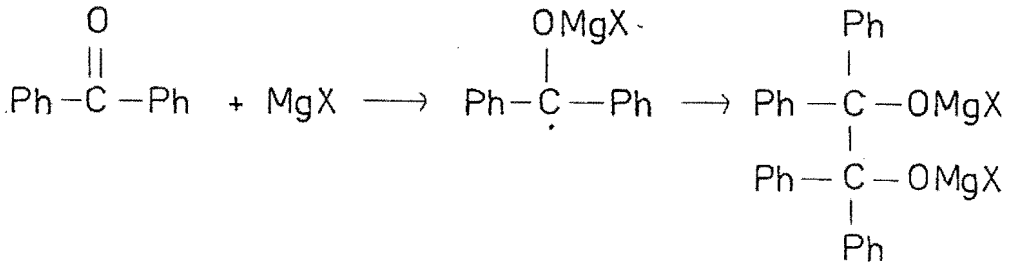
Scheme 28

reasonable, 1,3-diphenyl-3-methylbutan-1-ol(97a) was reacted with methylmagnesium iodide to form the alkoxide(98) which was allowed to react with benzaldehyde. 1,3-Diphenyl-3-methylbutan-1-one(92a) and benzyl alcohol(93) were isolated from this reaction.

The dimerisation of aromatic ketones to pinacols in Grignard reactions is again not unprecedented. Gomberg and Bachmann[55] found that the dimerisation of benzophenone(46) to benzopinacol(99) occurred when magnesous iodide(MgI) or magnesium-magnesium iodide($Mg-MgI_2$) was present in the reaction mixture. It was noted that magnesium iodide (MgI_2) alone was ineffective for this dimerisation. Bachmann and Shankland[56] suggested that MgX was involved and added to the carbonyl to give a ketyl radical which could be stabilised by

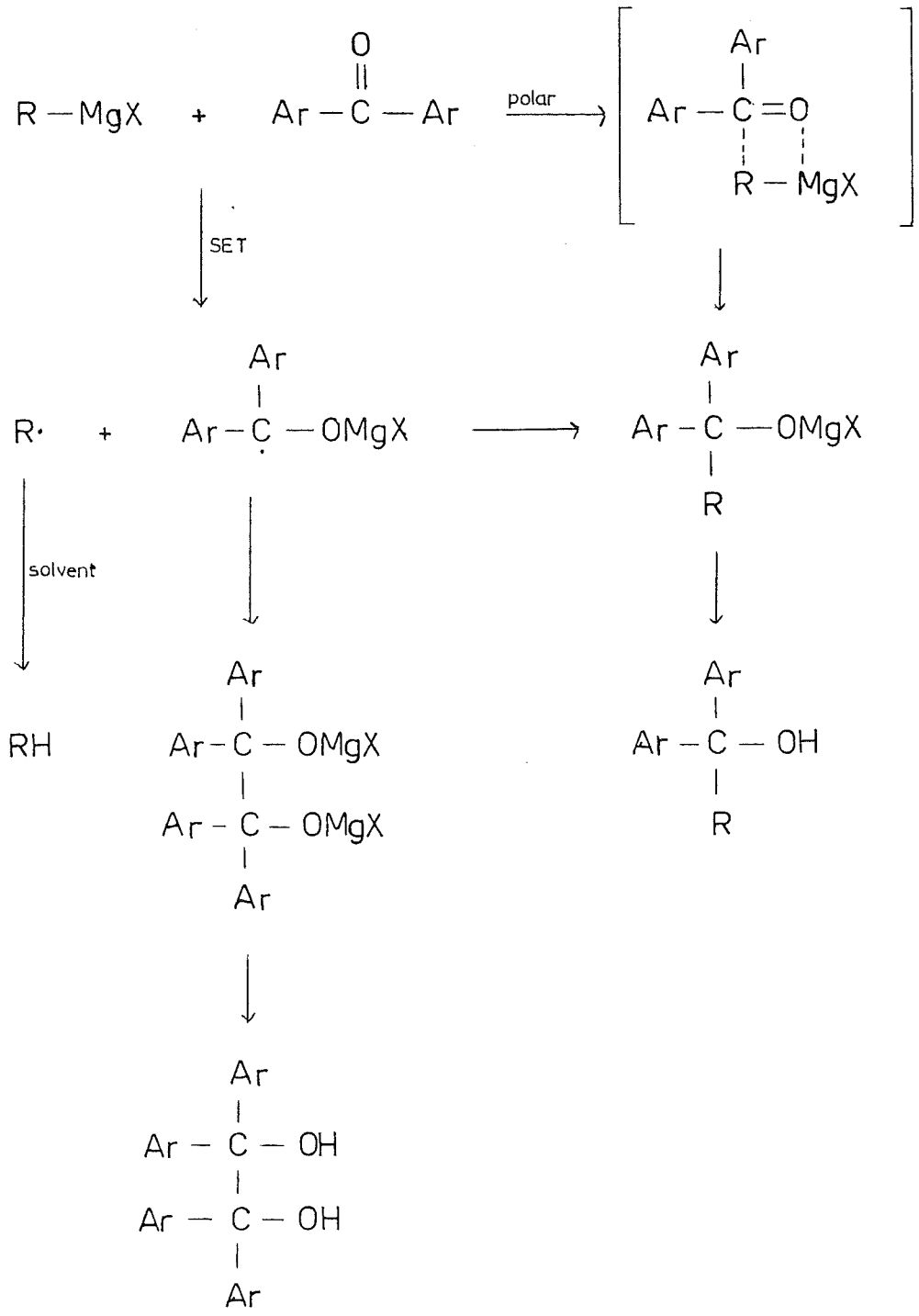


dimerisation(Scheme 29).

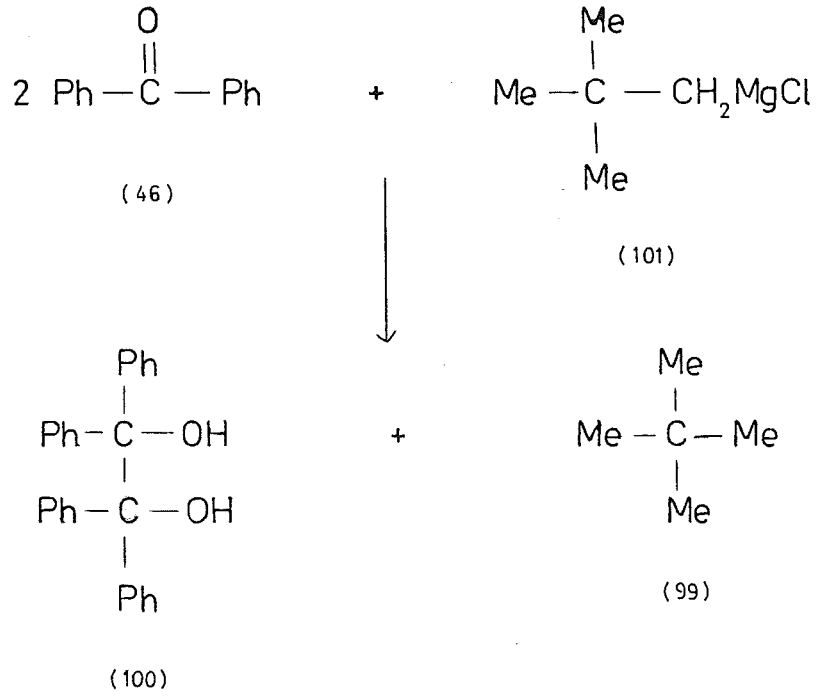


Scheme 29

More recently both the formation of pinacol and hydrocarbon products in Grignard reactions of aromatic ketones has been suggested by Ashby and his associates[57] to involve a single electron transfer process(Scheme 30). The mechanism they suggested again involves addition of MgX to the carbonyl and indeed they found some evidence from e.s.r. studies that these Grignard reactions give rise to radical intermediates. The alkyl radical may react with the ketyl radical to form the normal addition product or abstract a proton from the solvent to form a hydrocarbon. The isolation of benzopinacol(99) and neopentane(100) from the reaction of neopentylmagnesium chloride(101) and benzophenone(46) lends support to the proposed single electron

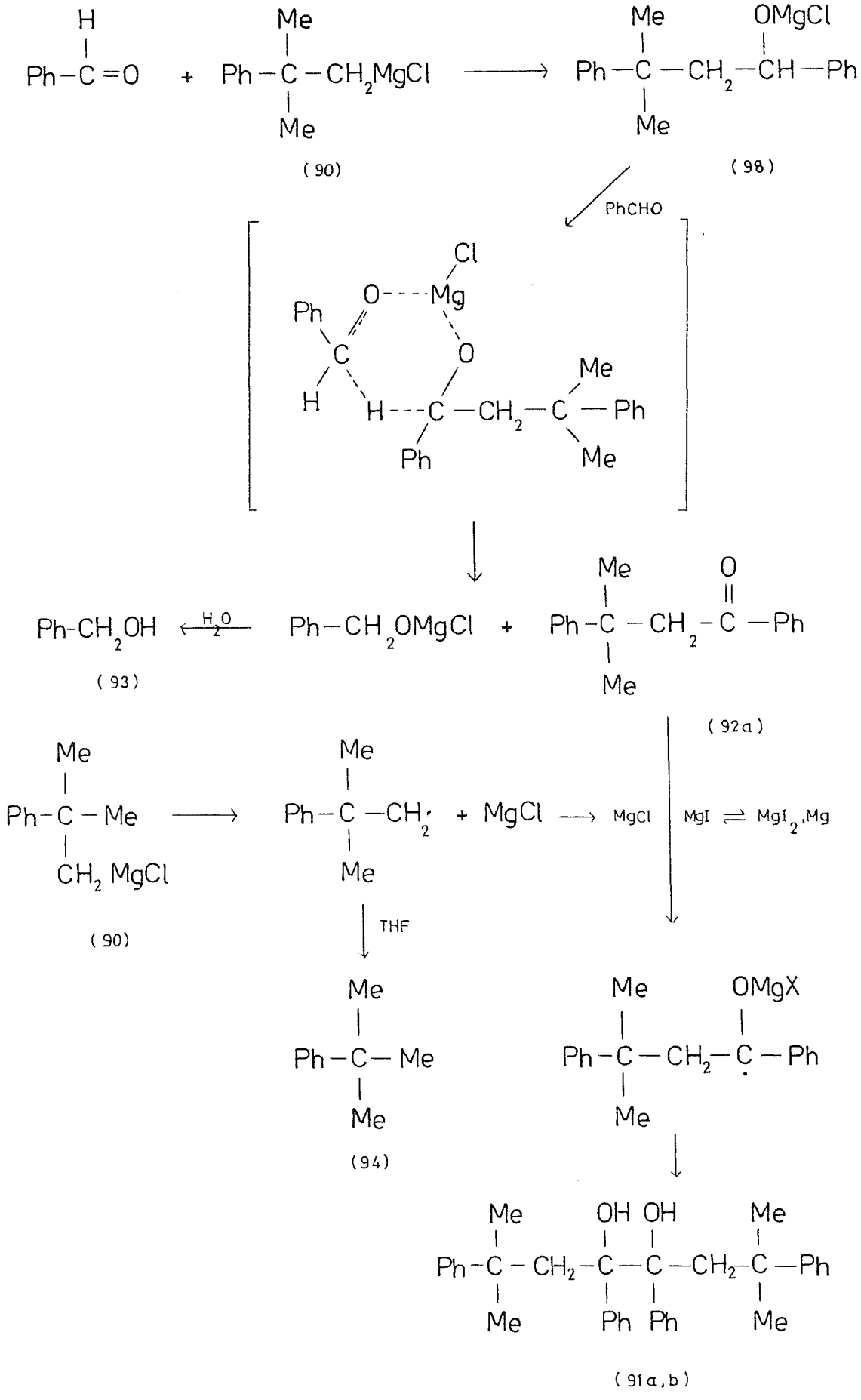


Scheme 30



transfer mechanism. In order to demonstrate that this mechanism could be involved in the formation of the diols (91a,b) during the reaction of benzaldehyde and 2-methyl-2-phenylpropylmagnesium chloride(90), 1,3-diphenyl-3-methylbutan-1-one(92a) was added to a stirred mixture of magnesium-magnesium iodide in dry ether. Heating this mixture under reflux resulted in the formation of the *dl* and *meso* diols (91a,b).

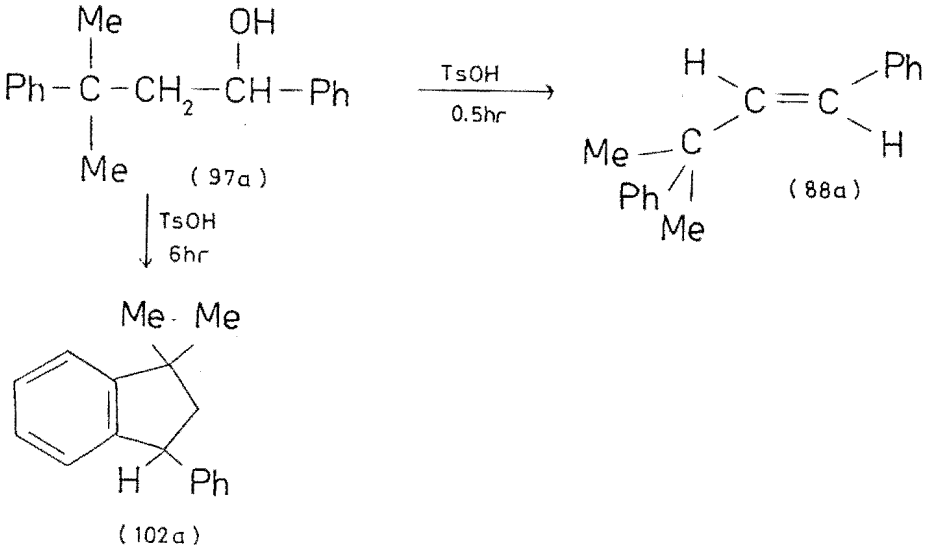
From these experiments, firstly the reaction of 1,3-diphenyl-3-methylbutan-1-ol(97a) with methylmagnesium iodide and benzaldehyde to give 1,3-diphenyl-3-methylbutan-1-one(92a), and secondly, the reaction of the ketone(92a) with magnesium-magnesium iodide to give the *dl* and *meso* diols (91a,b), the formation of 2,7-dimethyl-2,4,5,7-tetraphenyl-octane-4,5-diol(91) from benzaldehyde and 2-methyl-2-phenyl-propylmagnesium chloride(90) is considered to involve the



Scheme 31

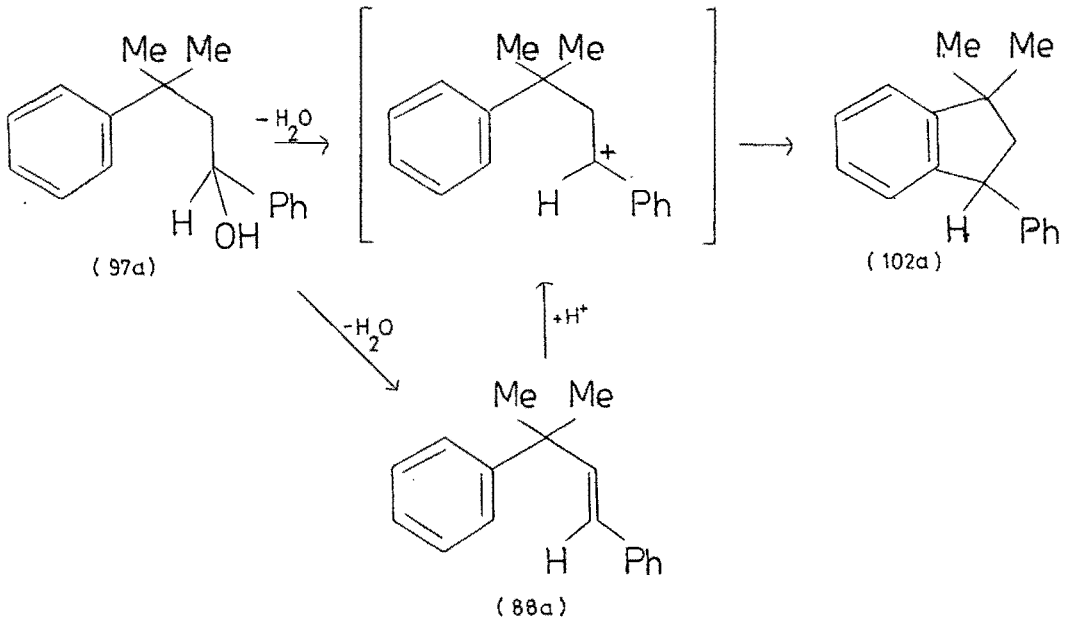
initial formation of the normal addition magnesium alkoxide product(98). Reaction of this alkoxide with benzaldehyde as shown in Scheme 31 accounts for the formation of the ketone(92a) and benzyl alcohol(93). Only if this mixture is heated does dimerisation of the ketone(92a) occur and this process requires the presence of $Mg-MgX_2$. If the dimerisation is a radical process and initiated by MgX, magneseous halide may be formed from reaction of excess magnesium metal with the magnesium iodide present. Iodine is used to initiate Grignard reagent formation. Alternatively, homolysis of the C-Mg bond of the Grignard reagent(90) would give MgCl. Under such circumstances the alkyl radical would be expected to abstract a hydrogen from the solvent THF and give an alkane. The formation of 2-methyl-2-phenylpropane(94) in the reaction of 2-methyl-2-phenyl-propylmagnesium chloride(90) with benzaldehyde in tetrahydrofuran is consistent with this process.

Zimmerman et al[58] have reported the dehydration of 1,3-diphenyl-3-methylbutan-1-ol(97a) by long term reaction with *p*-toluenesulphonic acid in benzene. In this study Zimmerman's procedure yielded not the required *trans*-1,3-diphenyl-3-methylbut-1-ene(88a) but gave 3,3-dimethyl-1-phenylindane(102a) as the only product. The indane(102a)



was identified from its ^{1}Hn.m.r. spectrum which was identical to that reported by Gelin[59] and showed two methyl groups as singlet peaks (δ_H1.20, 1.38) and a narrow multiplet centered at δ_H7.05 (Wh|2 3Hz) consistent with there being nine aromatic protons. The methylene protons appeared as a complex multiplet centered at δ_H2.13 (Wh|2 55Hz) due to both geminal and vicinal proton coupling. The methine proton appeared as a doublet of doublets (δ_H4.32, J 10Hz, J 7.5Hz) due to coupling from the neighbouring methylene protons.

The formation of the indane(102a) may involve the intermediacy of alkene(88a) by loss of H_2O and indeed in a

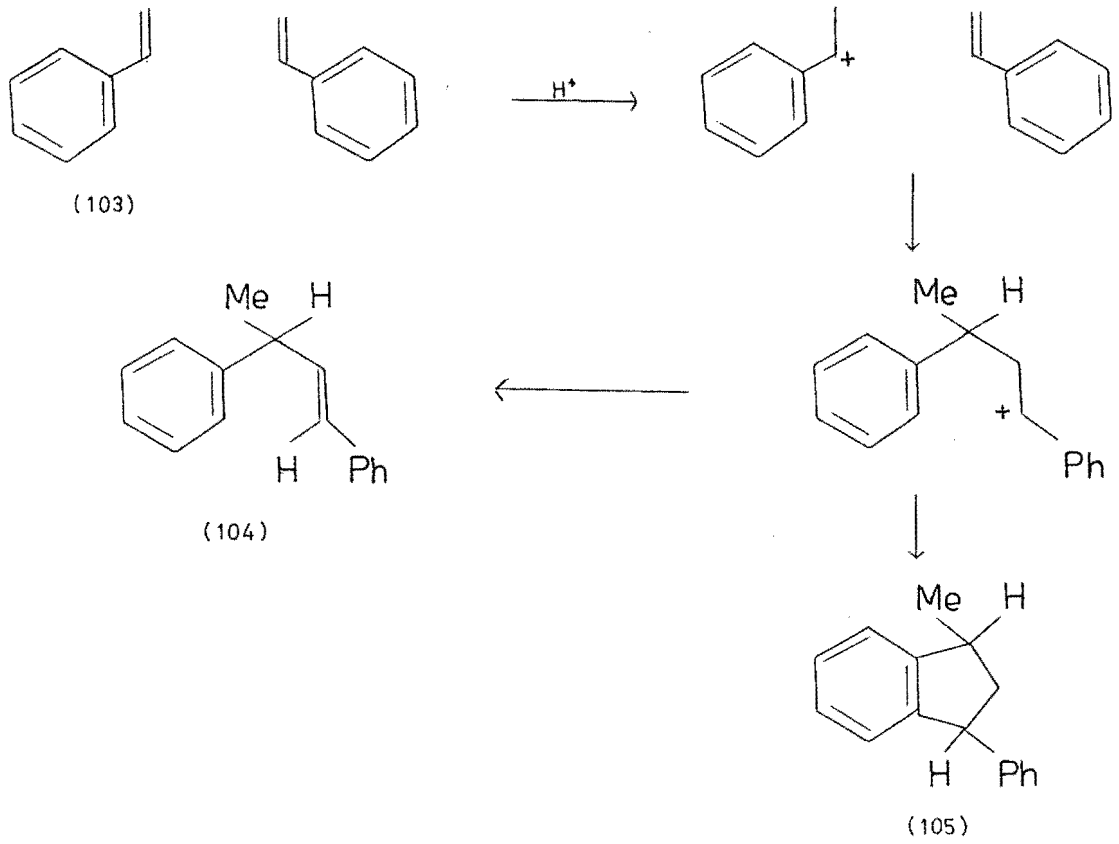


Scheme 32

separate experiment it was demonstrated that the alkene(88a) under these reaction conditions gave indane(102a). Protonation at C2 of the alkene(88a) and intramolecular electrophilic substitution accounts for the formation of the five-membered ring(Scheme 32).

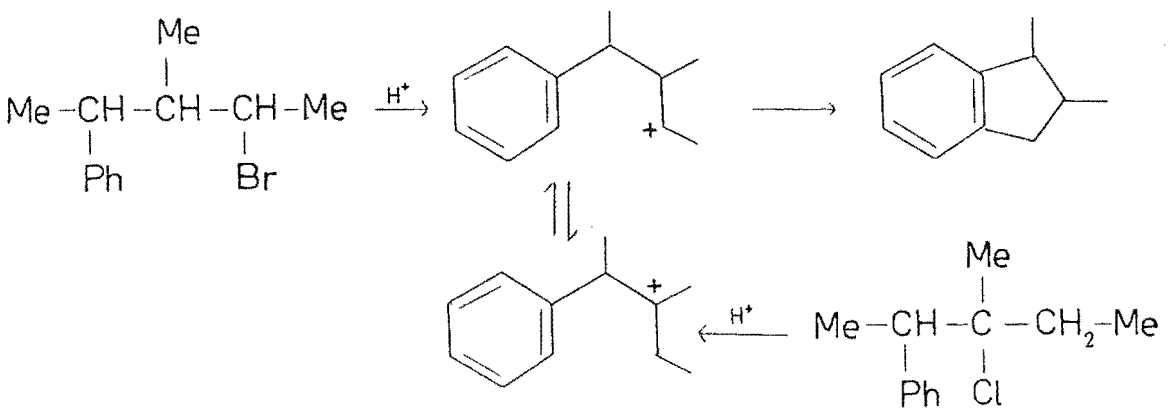
Formation of phenyl substituted indanes have been previously observed from dimerisation of styrene(103)[60]. Acid reaction with styrene(103) gives 1,3-diphenylbut-1-ene(104)

and 3-methyl-1-phenylindane(105) and it has been said that the reaction involves a benzylic cationic intermediate(Scheme 33). Intramolecular electrophilic substitution and formation



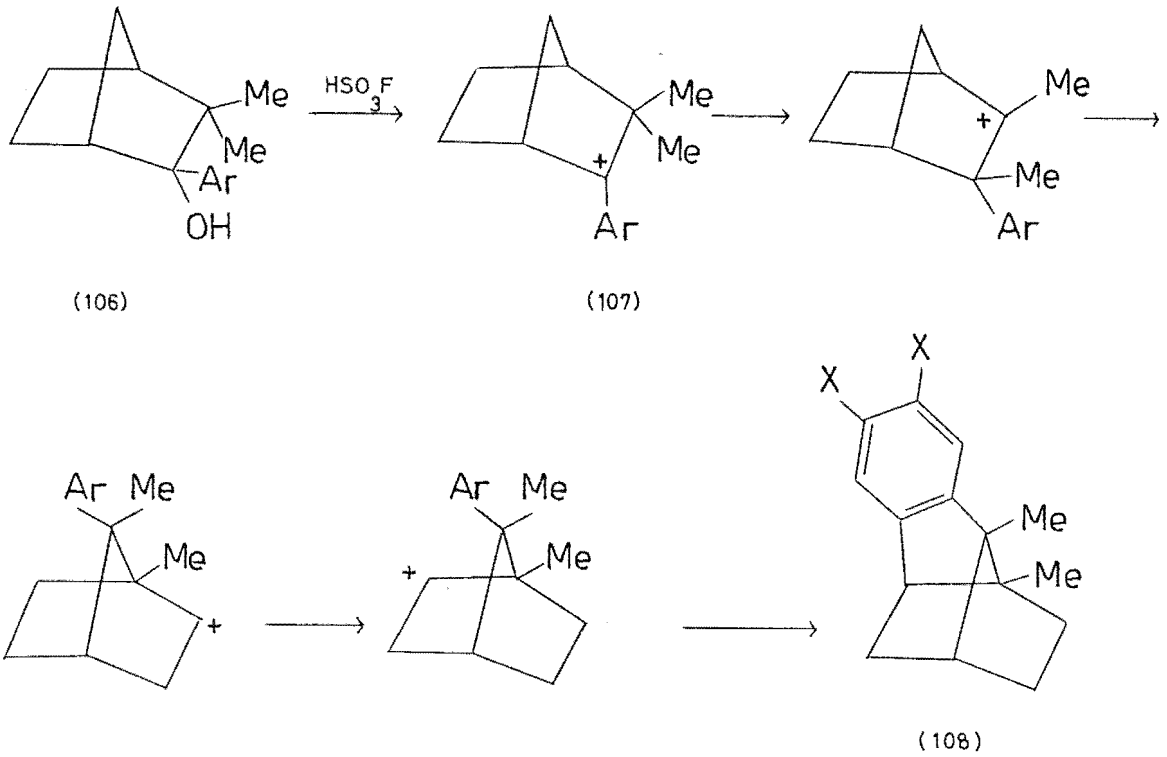
Scheme 33

of indane-type structures has also been observed to occur from cations generated by acid treatment of phenyl substituted alkyl halides(Scheme 34)[61] and those generated at low temperatures[62]. For example, 2-*exo*-aryl-3,3-dimethylbicyclo[2,2,1]heptan-2-*endo*-ols(106) on reaction with fluorosulphonic acid



Scheme 34

in sulphuryl chloride fluoride at low temperatures (from -90^{o} to c. $-20^{o}C$) give firstly 2-aryl-3,3-dimethylbicyclo [2,2,1]hept-2-yl cations(107) which on warming rearrange to



(106) (107) (108)

Scheme 35

7,8,12-trimethyl-tetracyclo[7,4,0,$0^{2,7}$, $0^{4,8}$]-trideca-1(9), 10,12-trienes(108) which under the reaction conditions are fluorosulphonated. With $HClO_4$ the parent hydrocarbons are formed. The formation of these compounds is shown in Scheme 35.

If 1,3-diphenyl-3-methylbutan-1-ol(97a) is allowed to react with *p*-toluene-sulphonic acid for only a short time (< ½hr), the required *trans*-alkene, 1,3-diphenyl-3-methylbut-1-ene(88a)[58], is formed in high yield. The structure of the olefin(88a) was confirmed by its i.r. spectrum which showed a *trans* carbon double bond stretch at ν 970 cm^{-1} and its ^{1}Hn.m.r. spectrum in which the two methyl groups appeared as a single peak (δ_H1.45), the two vinyl protons as a single peak (δ_H6.36) and the two phenyl groups as a narrow multiplet

(δ_H7.28, Wh|2 2Hz). No *cis*-1,3-diphenyl-3-methylbut-1-ene (109a) could be detected.

Having determined the optimum reaction conditions for the formation of the alcohol(97) and alkene(88), a series of five substituted (b,*p*-PhOMe; c, *p*-PhMe; d, *p*-PhCl; e, *m*-PhCl; f, 3′,4′-$PhCl_2$)1-aryl-3-methyl-3-phenylbutanols(97b-f) were prepared by reaction of appropriately substituted aldehydes with 2-methyl-2-phenyl-propylmagnesium chloride(90)(Scheme 22). The structures of the products were confirmed by ^{1}Hn.m.r., ^{13}Cn.m.r. and mass spectra, Reaction of the alcohols(97b-f) with *p*-toluenesulphonic acid gave the required *trans*-1-aryl-3-methyl-3-phenylbut-1-enes(88b-f) which were identified from their ^{1}Hn.m.r. and ^{13}Cn.m.r. spectra and by comparison with those of the parent alkene(88a). In no case was there any evidence for the formation of *cis*-alkene(109b-f).

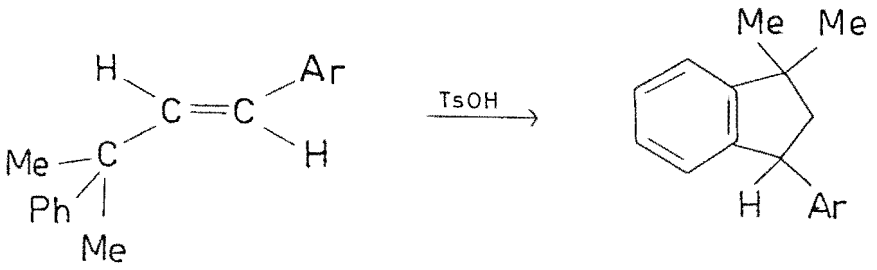
The *p*-cyano substituted alkene(88g) was formed by the reaction of *trans*-1-(4′-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d) with cuprous cyanide in N-methyl-2-pyrrolidone.

The alkenes(88b-f) all formed indanes(102b-f) on prolonged treatment with *p*-toluenesulphonic acid. However, the yield of the product depended on the aryl substituent and the length of time of reaction (Table 1). During the course of these studies, the deuterated alkene(110c) was required, and this alkene,on extended reaction with *p*-toluenesulphonic acid, gave the deuterated indane(111), not surprisngly with no loss of deuterium at Cl. This therefore excludes C2-Cl hydride shifts in any intermediate benzyl cation. The ^{1}Hn.m.r. spectrum of the deuterated indane(111) showed the Cl-methyl groups as two peaks (δ_H1.24, 1.40) and the aryl substituted methyl group as another single peak (δ_H2.31). The complex multiplet observed

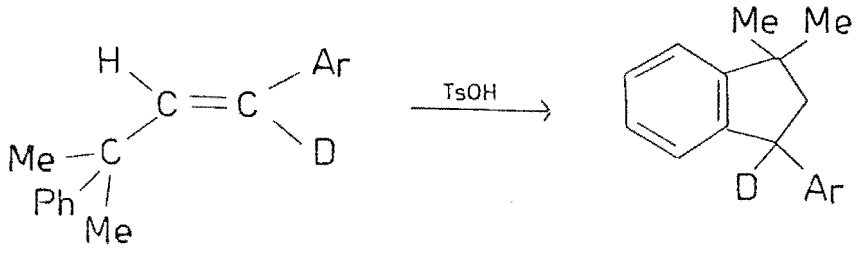
TABLE 1

Formation of Indane(102) from Alkene(88)

Cl-aryl substituent	Reaction Time (hr.)	Percentage Indane
p-PhOMe	4.5	100 %
p-PhMe	3.5	66 %
PhH	6	100 %
p-PhCl	6	17 %
m-PhCl	22	96 %
3',4'-$PhCl_2$	18	38 %



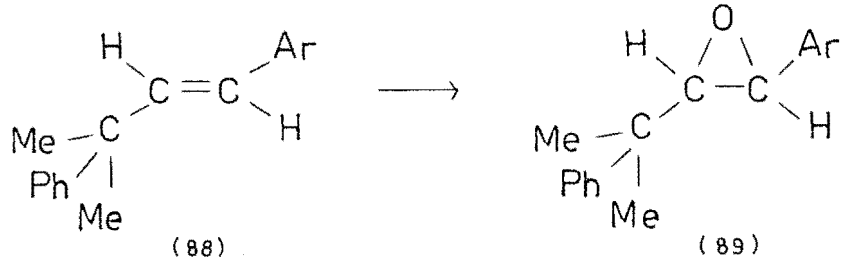
(88) (102)



(110c) (111)

at δ_H2.18 (Wh|2 29Hz) for the two methylene protons in the undeuterated indane(102c), was simplified in the deuterated analogue(111) and appeared as an AB quartet (δ_H1.94, 2.36, J 12Hz). The signal due to H3 centered at δ_H4.28 in the undeuterated analogue was notably absent.

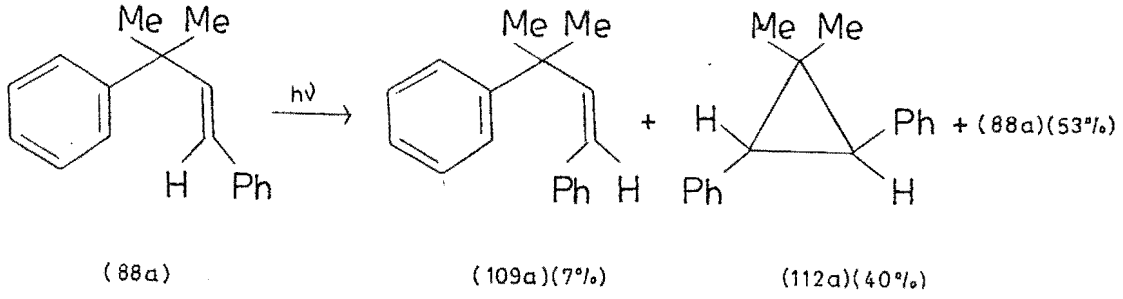
The reaction of *trans*-1,3-diphenyl-3-methylbut-1-ene (88a) with *m*-chloroperbenzoic acid afforded *trans*-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a) in 60% yield. The presence of the epoxide moiety was confirmed by the infrared spectrum which showed a C-O-C stretch at ν 1245 cm^{-1}. The ^{1}Hn.m.r spectrum showed two methyl signals (δ_H1.32, 1.41) and a narrow multiplet due to the ten aromatic protons (δ_H7.32, Wh|2 2Hz). The epoxide protons appeared as an AB quartet (δ_H3.02, 3.73, J 2Hz). The H1, H2 coupling constant, J = 2Hz, confirmed the *trans* nature of the epoxide[63] and hence the *trans* nature of the alkene precursor.



The C1-aryl substituted epoxides(89b-f) were similarly prepared by the reaction of the alkenes(88b-f) with *m*-chloroperbenzoic acid. The epoxides(89b-f) were identified by comparison of their spectral data with those obtained for *trans*-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a). The H1, H2 coupling (J 2.5Hz) observed in the ^{1}Hn.m.r. spectrum of each showed that only the *trans* epoxides were formed.

Photolysis of *trans*-1-Aryl-3-methyl-3-phenylbut-1-enes

The series of substituted *trans*-1-aryl-3-methyl-3-phenylbut-1-enes(88a-g) were prepared as previously described and their photochemistry was investigated. The photochemistry of the parent olefin(88a) in this series has been reported by Zimmerman[58] to give *cis*-1,3-diphenyl-3-methylbut-1-ene(109a) (7%) and *trans*-3,3-dimethyl-1,2-diphenylcyclopropane(112a) (40%) but no *cis*-3,3-dimethyl-1,2-diphenylcyclopropane(113a) was detected.



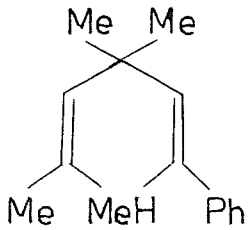
(88a) (109a)(7%) (112a)(40%)

This reaction was repeated in order to have samples of the reaction products. Photolysis of *trans*-1,3-diphenyl-3-methylbut-1-ene(88a) in *t*-butyl alcohol for 0.25hr and 0.5hr gave *cis*-1,3-diphenyl-3-methylbut-1-ene(109a) (c.4 and 4% respectively), *trans*-3,3-dimethyl-1,2-diphenylcyclopropane(112a) (c.29 and 64% respectively) and unreacted *trans*-olefin(88a) (c.67 and 32% respectively). The ^{1}Hn.m.r. spectrum of *trans*-3,3-dimethyl-1,2-diphenylcyclopropane(112a) showed the two methyl groups in identical chemical environments with peaks centered at δ_H0.96, the two cyclopropyl protons as a singlet at δ_H2.31 and the aromatic protons resonating at δ_H7.28. The ^{1}Hn.m.r. spectrum of *cis*-1,3-diphenyl-3-methylbut-1-ene(109a) showed the two methyl groups as a peak at δ_H1.33, the two vinyl protons as

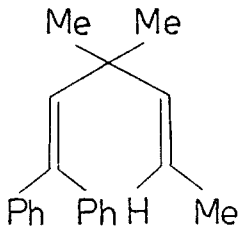
an AB quartet (δ_H5.76, 6.37, J 13Hz) and ten aromatic protons resonating at δ_H7.05.

The isomerisation of *trans*-alkenes to *cis*-alkenes is a reversible reaction which may proceed from the S_1 or T_1 excited states and in the absence of any competing photochemical pathways, a photostationary state between *cis* and *trans* isomers is established[64]. Sensitisation with *m*-methoxy-acetophenone of the photolysis reaction of *trans*-1,3-diphenyl-3-methylbut-1-ene(88a)[58] resulted in the formation of the *cis*-alkene(109a) as the only product. From the absence of cyclopropane products in the photosensitised reaction it can be assumed that cyclopropane derivatives are formed from the S_1 excited state. Formation of the *cis*-alkene from the S_1 excited state is of course not precluded by this experiment. In the unsensitised photolysis of the *trans*-alkene(88a) formation of *trans*-3,3-dimethyl-1,2-diphenylcyclopropane(112a) competes with *cis-trans* isomerisation and the photostationary equilibrium of the alkene is disturbed.

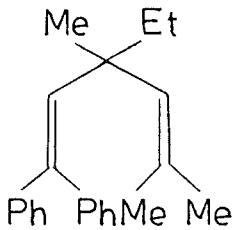
The stereochemistry of the di-π-methane rearrangement in the divinyl methane systems (13)[7], (9)[5] and (12)[65] has



(13)



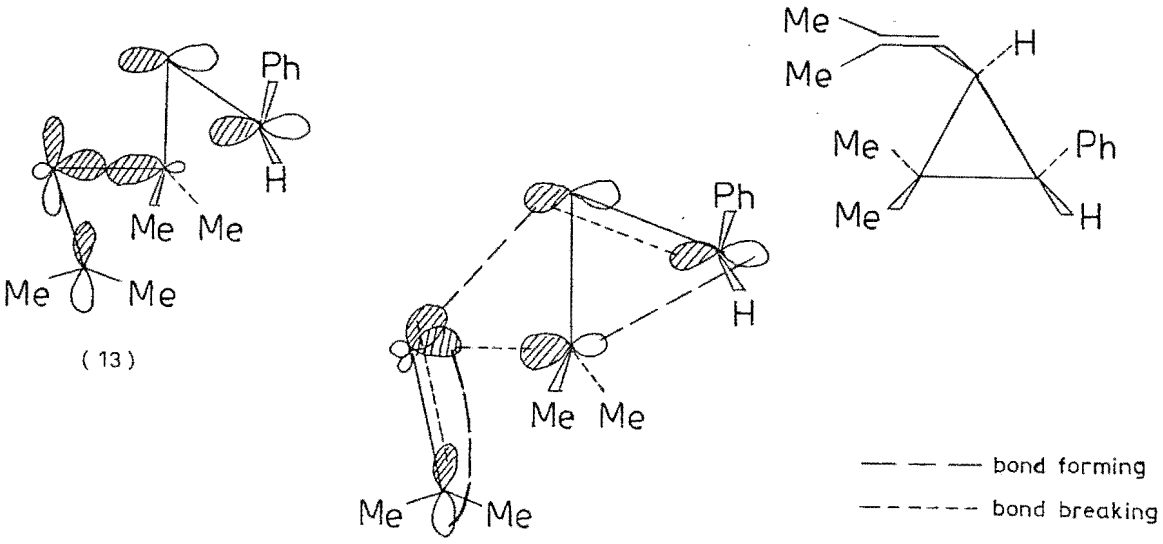
(9)



(12)

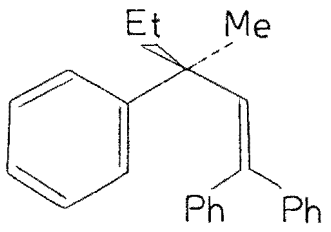
been shown to involve retention of configuration at C1 and C5 and inversion at C3 respectively. The overall reaction pathway can be described by a Möbius array of atomic orbitals

where the bonds breaking and bonds forming conform to the observed stereochemistry(Scheme 36). Similar studies on the



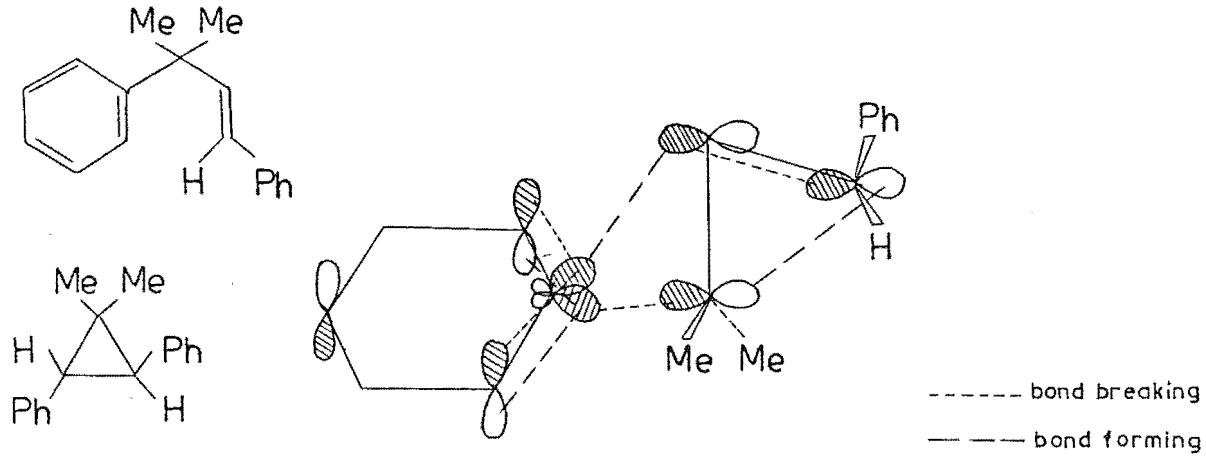
Scheme 36

aryl-vinyl methane system(114)[66,67] have shown that



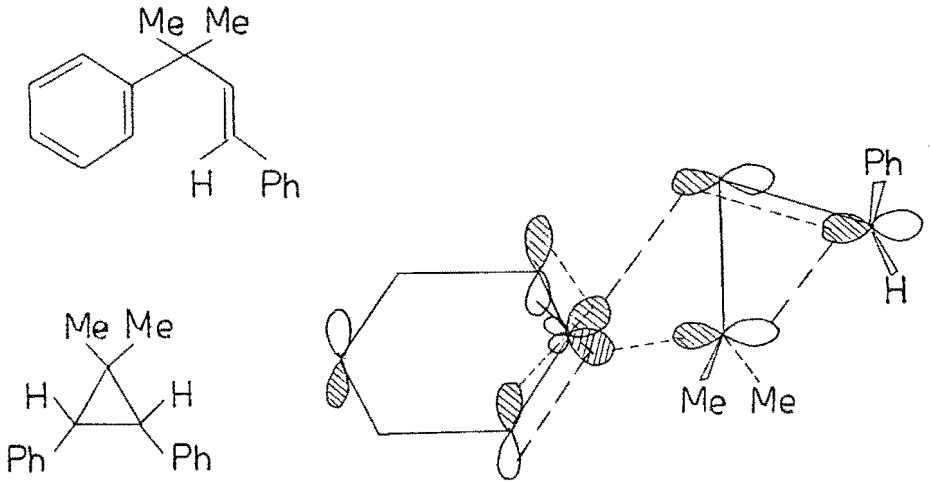
(114)

the rearrangement occurs for this system with inversion of configuration at C3 and the formation of the *trans*-cyclopropane(112a) on the photolysis of *trans*-1,3-diphenyl-3-methyl-but-1-ene(88a)[58] shows that the reaction proceeds with retention of configuration at C1. A Möbius array analogous to that drawn for the divinyl system can be written for the aryl-vinyl rearrangement. For this system a molecular orbital involving the migrating aromatic ring replaces the second π system of the divinyl molecule(Scheme 37). Formation of a *trans*-cyclopropane from a *trans*-alkene is an



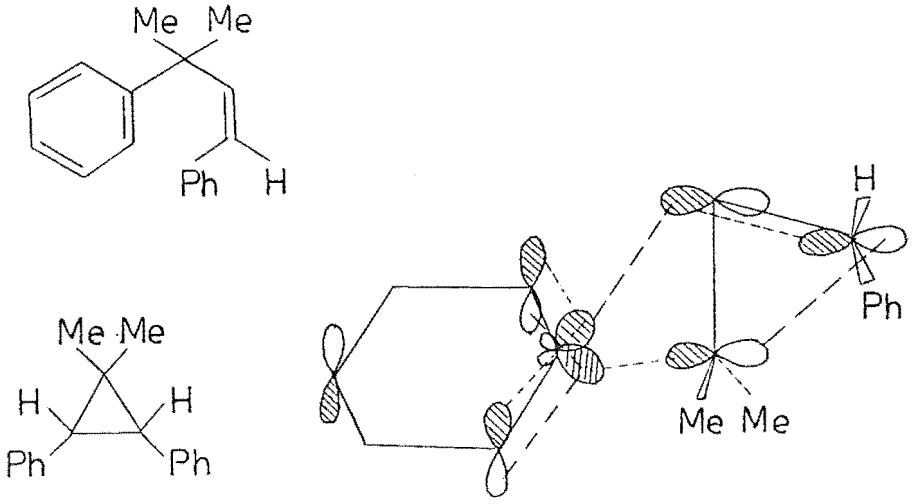
Scheme 37

allowed photochemical reaction as the Möbius array has only one +- node. The formation of a *cis*-cyclopropane from a *trans*-alkene as depicted in the Möbius array(Scheme 38)



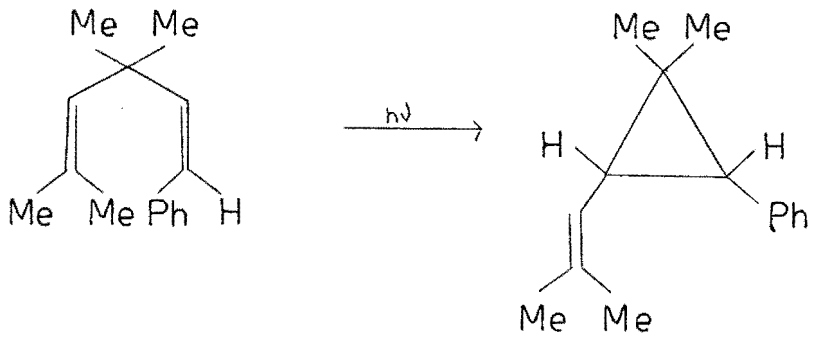
Scheme 38

requires inversion at C1 and results in two +- nodes, a photochemically disallowed rearrangement. Formation of the



Scheme 39

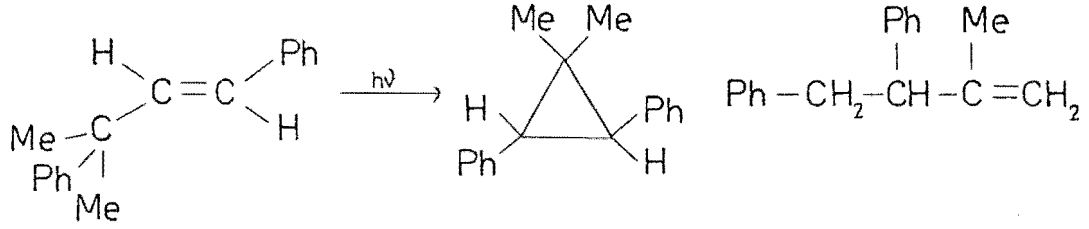
cis-cyclopropane from a *cis*-alkene is allowed photochemically (Scheme 39) but Zimmerman found that photolysis of *cis*-1,3-diphenyl-3-methylbut-1-ene(109a) resulted in the formation of *trans*-alkene(88a) only. The absence of cyclopropane formation from the *cis*-alkene(109a) may be due to steric hindrance for ring closure although the same interference does not prevent *cis*-cyclopropane formation in the analogous divinyl system(Scheme 40)[7]. Alternatively *cis-trans*



Scheme 40

isomerisation may be too fast for cyclisation to occur.

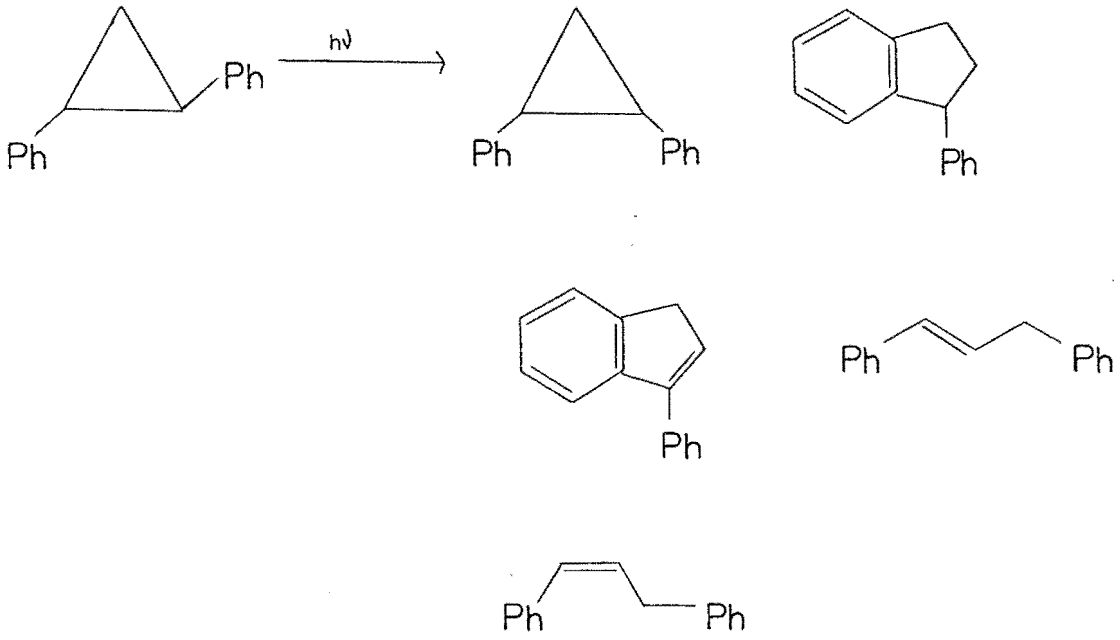
In a longer term photolysis reaction (6hr) of the *trans*-olefin(88a) in *t*-butyl alcohol, *trans*-3,3-dimethyl-1,2-diphenylcyclopropane(112a) (71%) and 3,4-diphenyl-2-methylbut-1-ene(115a) (29%) were isolated. No *cis*- or *trans*-1,3-diphenyl-3-methylbut-1-ene(88a,109a) could be



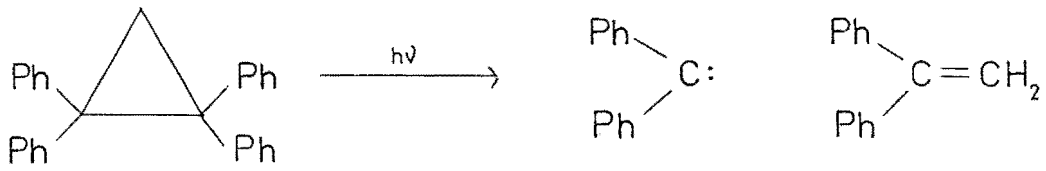
(88a) (112a)(71%) (115a)(29%)

detected by ^{1}Hn.m.r. spectroscopy of the crude reaction mixture. The structure of the secondary photoproduct, 3,4-diphenyl-2-methylbut-1-ene(115a) was determined from its ^{1}Hn.m.r. and ^{13}Cn.m.r. spectra. A broad signal at δ_H4.88 (Wh$|_2$ 8Hz) indicated the presence of terminal vinyl protons. The singlet peak at δ_H1.60 showed the presence of one vinyl methyl group and a narrow multiplet (Wh$|_2$ 3Hz) at δ_H7.10 indicated the presence of two phenyl rings. A wide multiplet centered at δ_H3.28 (Wh$|_2$ 27Hz) represented the neighbouring C3H and C4H$_2$. The ^{13}Cn.m.r. showed these carbon signals centered at δ_C54.4 and δ_C39.9 respectively, the methyl group resonance at δ_C21.5, the terminal vinyl carbon peak at δ_C110.8 and C2 at δ_C145.3. The two phenyl rings gave seven signals (C3Ar:δ_C142.9, 128.1, 128.0, 126.2; C4Ar:δ_C140.5, 129.9, 128.0, 125.7). In a separate experiment it was shown that prolonged photolysis of *trans*-3,3-dimethyl-1,2-diphenylcyclopropane(112a) gave 3,4-diphenyl-2-methylbut-1-ene(115a).

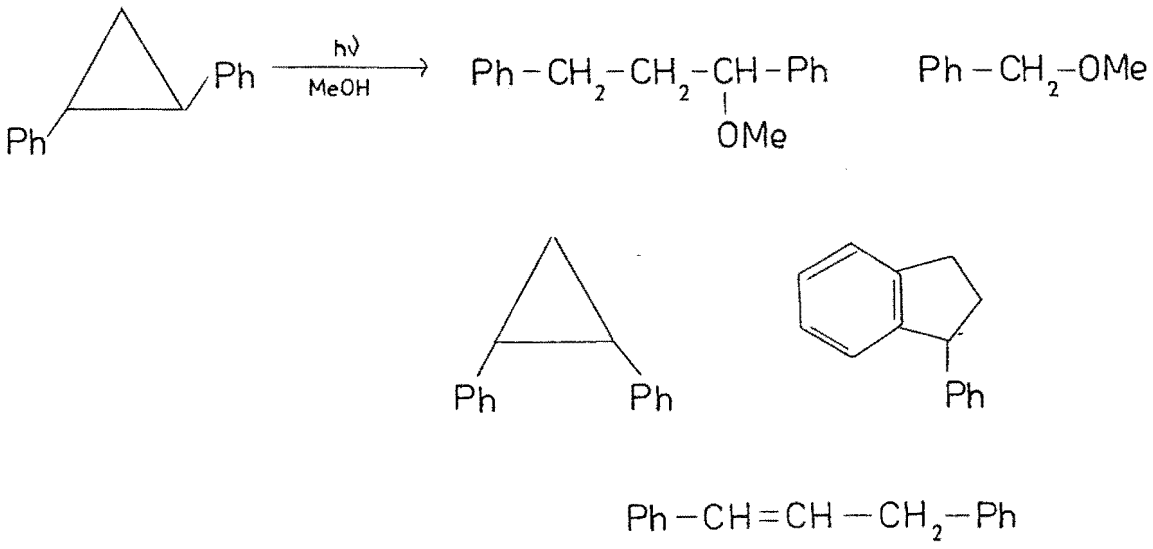
The known photochemistry of phenylcyclopropanes is characterised by four general processes; the first three processes, geometric isomerisation(Scheme 41)[68], fragmentation to carbenes(Scheme 42)[69] and addition of aprotic solvents (Scheme 43)[70] will not be discussed further. The remaining process, structural isomerism involving hydrogen migration is illustrated in Scheme 44. Kristinsson and Griffin[71] found that conversion of alkyl substituted phenylcyclopropanes to olefins was extremely efficient. Their study included the photolysis of the series of cyclopropanes for which R_1, R_2 and R_3 were hydrogen or methyl groups. They found that the conversions involved homolysis of the weakest bond of the cyclopropane ring followed by either intramolecular 1,4-transfer of a 1^{o} hydrogen atom from a methyl group to



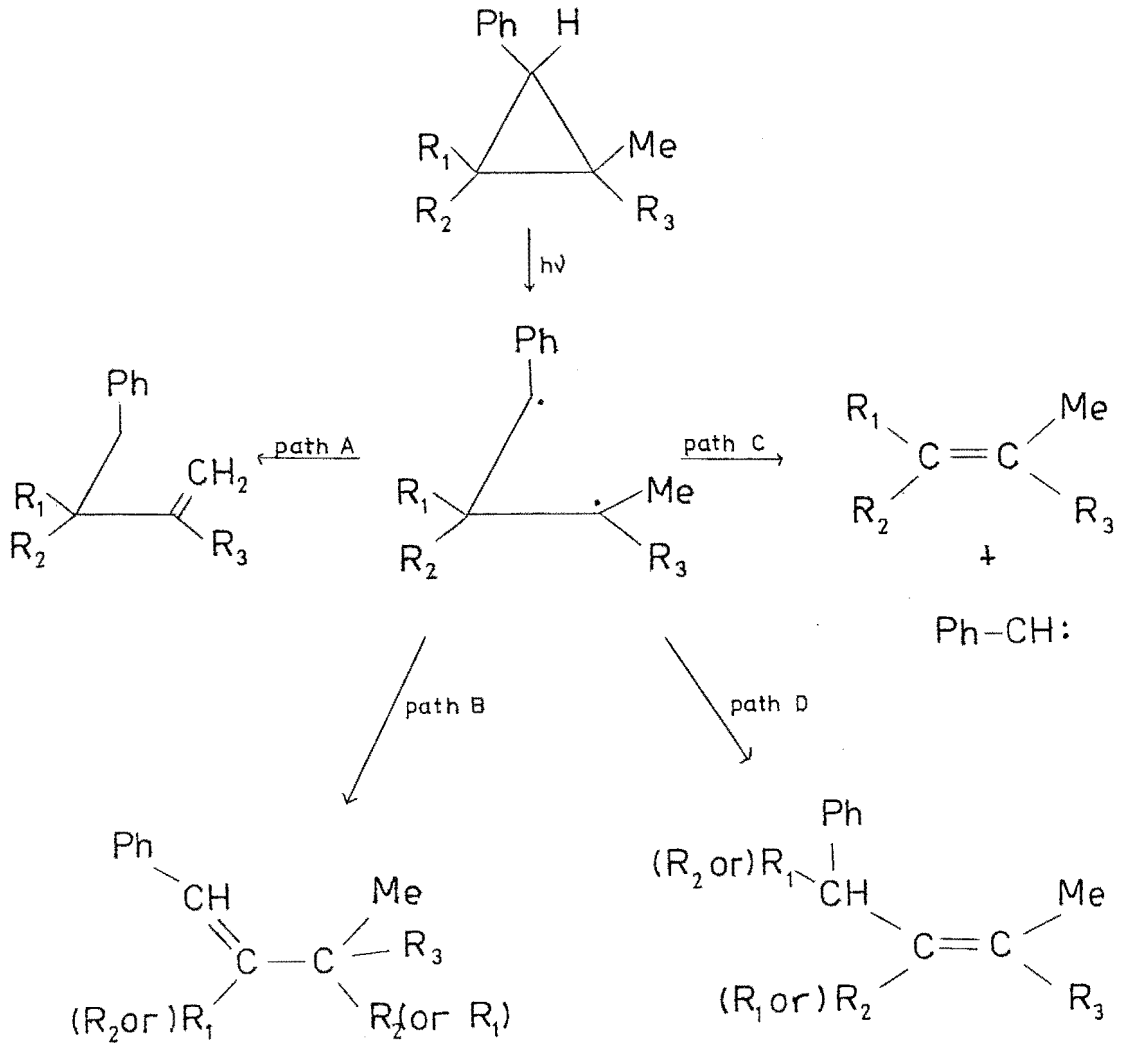
Scheme 41



Scheme 42



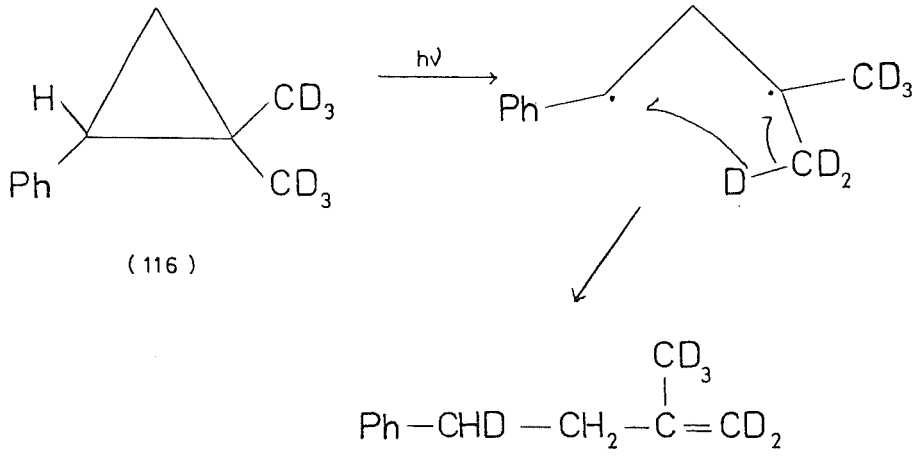
Scheme 43



Scheme 44

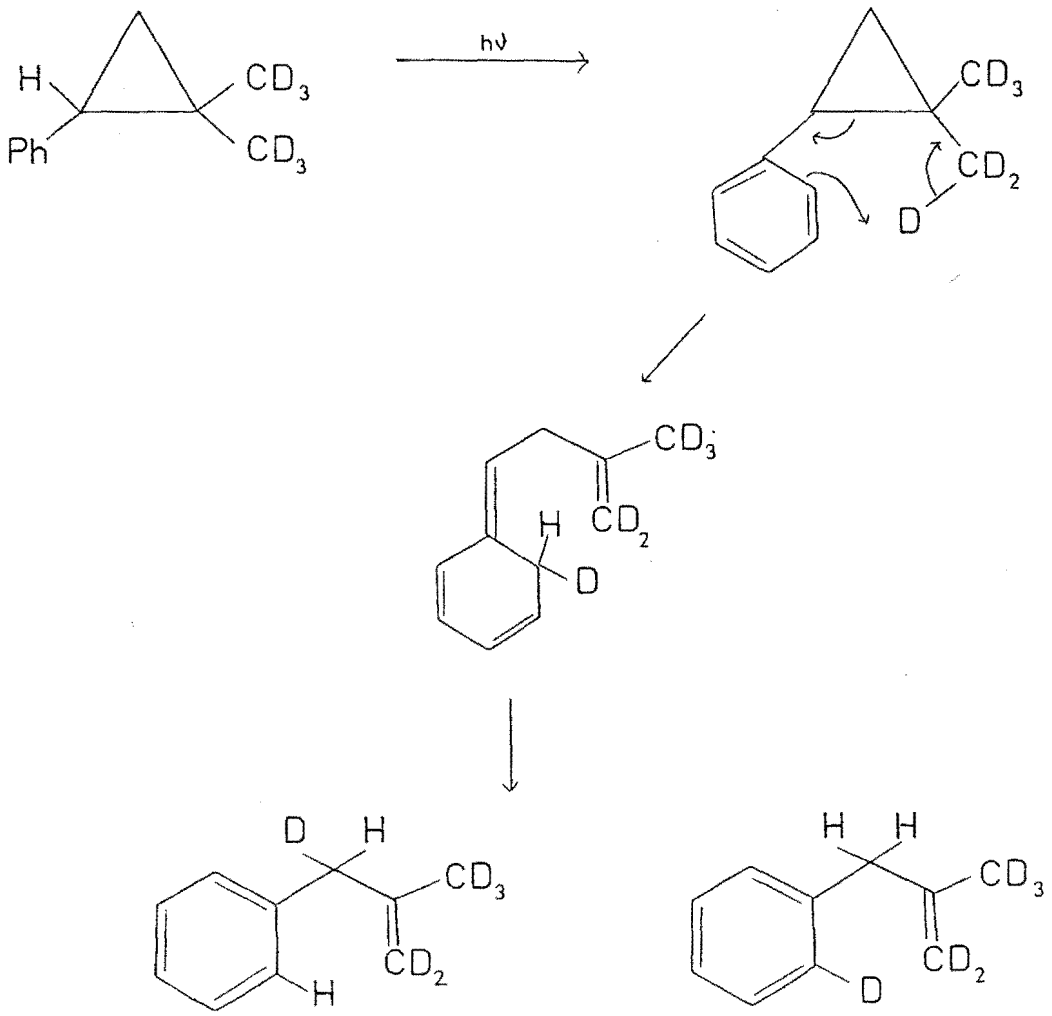
give a terminal olefin (path A) or 1,2-migration of a 3^{o} hydrogen to give a conjugated olefin (path B). Fragmentation to form carbenes (path C) and group migration (path D) to the more stable radical center was not observed.

Mazzocchi and Lustig[72] studied the photolysis of the deuterated derivative of 2,2-dimethyl-1-phenylcyclopropane(116) in order to elucidate the mechanism of terminal olefin formation. A diradical intermediate can be formed and stabilised by 1,4-hydrogen migration(Scheme 45). Alternatively, hydrogen migration may occur to the *ortho* position of the aromatic ring, followed by 1,3-hydrogen migration and rearomatisation(Scheme 46). A third possibility is that reaction occurs by a concerted $[\sigma^2_s + \sigma^2_s]$ mechanism(Scheme 47).

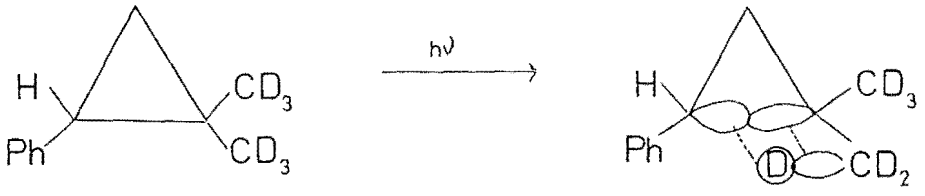


(116)

Scheme 45



Scheme 46

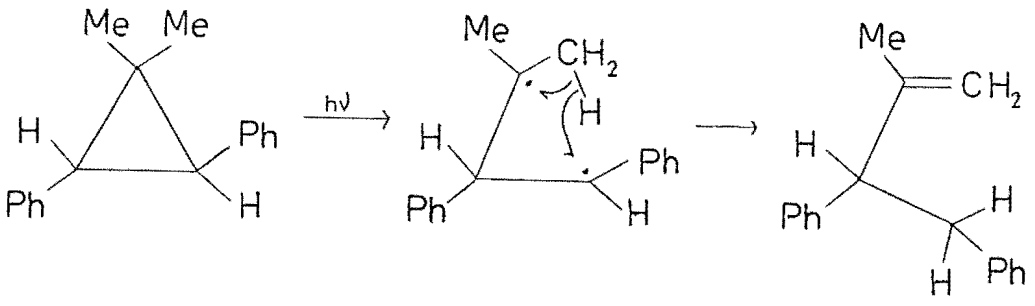


$$Ph-CHD-CH_2-\overset{\overset{CD_3}{|}}{C}=CD_2$$

Scheme 47

The formation of a diradical intermediate was excluded since a preference for hydrogen migration from the methyl group *trans* to the phenyl ring and retention of configuration at the migration terminus was observed. This excludes free rotation after cyclopropane ring bond cleavage. Hydrogen transfer to the *ortho* position of the phenyl ring was also excluded because no deuterium could be detected on the aromatic ring of the product from photolysis of (116). The preference for migration of hydrogen on the methyl *trans* to the phenyl group with retention of configuration is consistent with the $[\sigma^2_s + \sigma^2_s]$ transition state. Migration from the methyl *cis* to the phenyl ring would be hindered by the phenyl ring. However, this evidence does not exclude the mechanism which involves a diradical intermediate but, for that to be the case, rotation about the C2-C3 bond must be slow relative to hydrogen transfer.

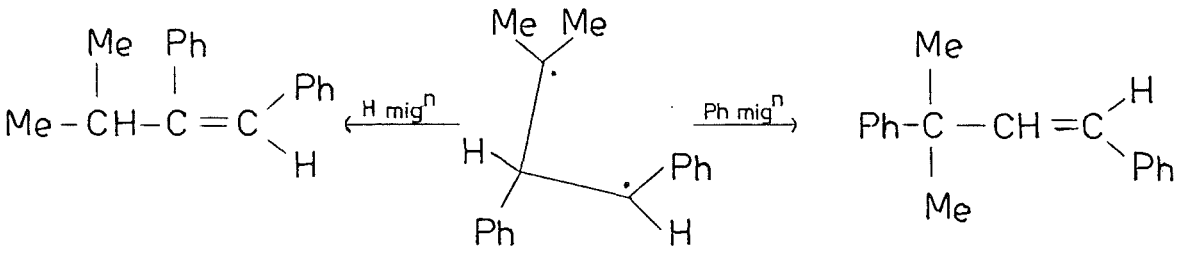
In the photolysis of *trans*-3,3-dimethyl-1,2-diphenylcyclopropane(112a), the only product formed was 3,4-diphenyl-2-methylbut-1-ene(115a) and for simplicity this is shown as occurring *via* a diradical intermediate(Scheme 48). 1,3-Diphenyl-3-methylbut-1-ene(88) and 1,2-diphenyl-3-methylbut-1-ene(117), the products expected from 1,2-group



(112a) (115a)

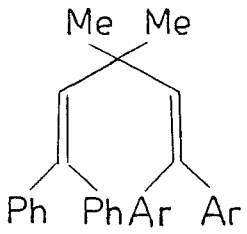
Scheme 48

migration of phenyl and hydrogen respectively, were not detected, showing that 1,4-hydrogen transfer is a more favoured process.



(117) (88)

Among the many studies carried out to elucidate the mechanism of the di-π-methane rearrangement, the effect of substituents, either bonded to the aryl groups which were attached to the vinyl carbon or bonded directly to the vinyl carbon, has played an important role. In particular substituent effects have provided evidence for polar intermediates[73].



(118)

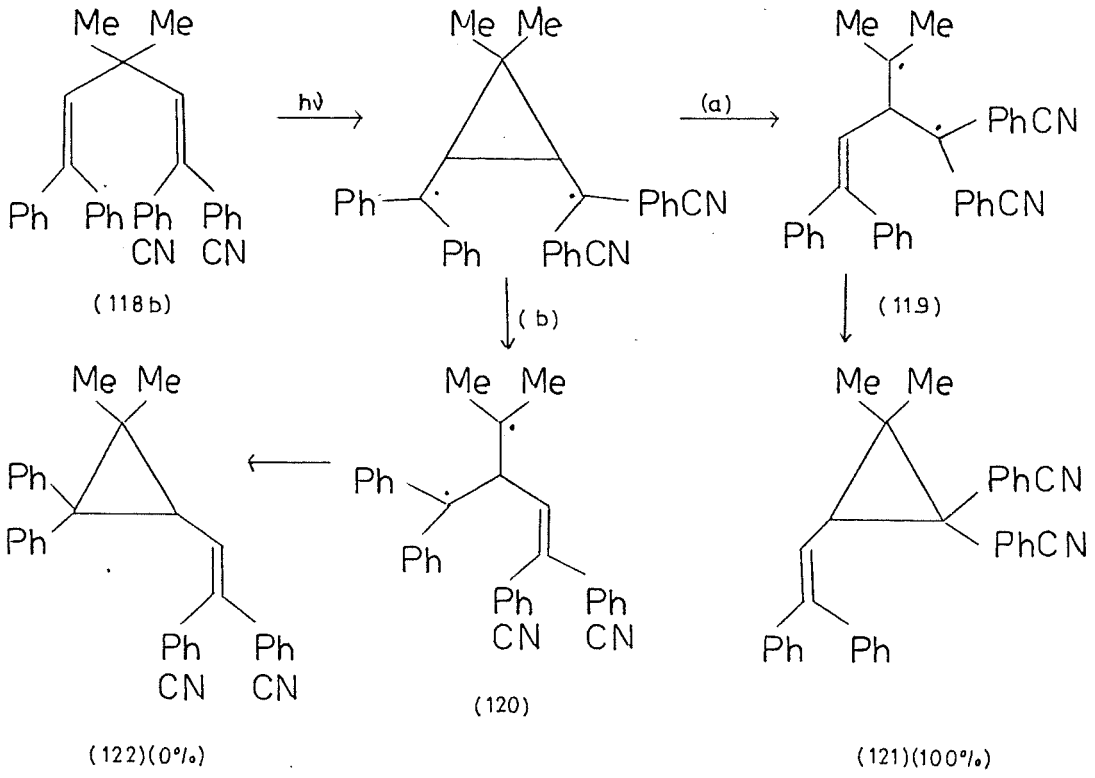
Ar: (a) p-Ph-OMe
(b) p-Ph-CN

For the above tetra-aryl substituted divinyl system(118) the rate of formation of the cyclopropane product(s) was found to be inhibited by *para* substituted electron donating groups (OMe)(118a) and accelerated by electron withdrawing substituents (CN)(118b)[74]. The absolute rates of rearrangement were determined using the equation below, where k_f, the rate of

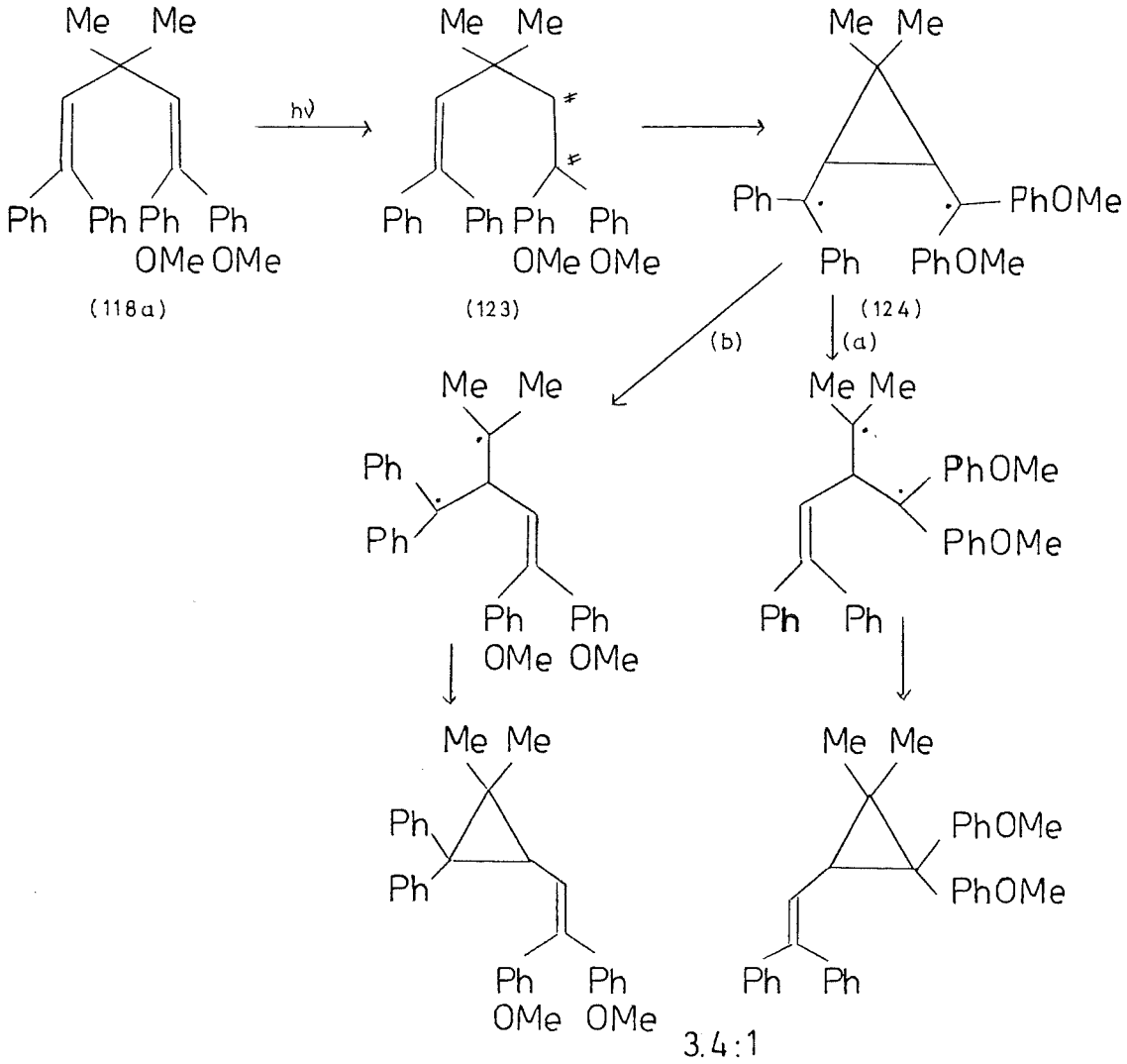
$$k_r = \frac{\Phi_r \; k_f}{\Phi_f}$$

fluorescence was determined from the emission spectrum, Φ_f, the quantum yield of fluorescence was determined relative to that of diphenylethylene and Φ_r, the quantum yield of the rearrangement was determined by isotope dilution where the disappearance of carbon-14 and tritium labelled reactants and the appearance of the labelled products was measured with a Bausch and Lomb monochromotor.

The regiospecificity observed with *para*-cyano substitution(118b) is attributed to the better electron delocalisation by a dicyanobenzhydryl moiety in diradical(119) than a benzhydryl moiety in diradical(120). The reaction mechanism is depicted in a stepwise fashion in Scheme 49. The dicyanobenzhydryl radical(119) is formed in preference to the benzhydryl radical(120) and this results in the incorporation of the cyano-substituted aryl rings in the three-membered ring(121). The rate acceleration observed for the cyano-substituted diene(118b) is thought to be due to the increased exothermicity of the bridging step relative to the unsubstituted phenyl derivative[75]. If this reaction mechanism is correct, then a similar effect on regioselectivity and rate should be observed for the *para*-methoxy diene(118a). However, for diene(118a) the rate of reaction decreases and the reaction is less specific(Scheme 50). For an odd-electron mechanism, path(a) should be preferred because a methoxy



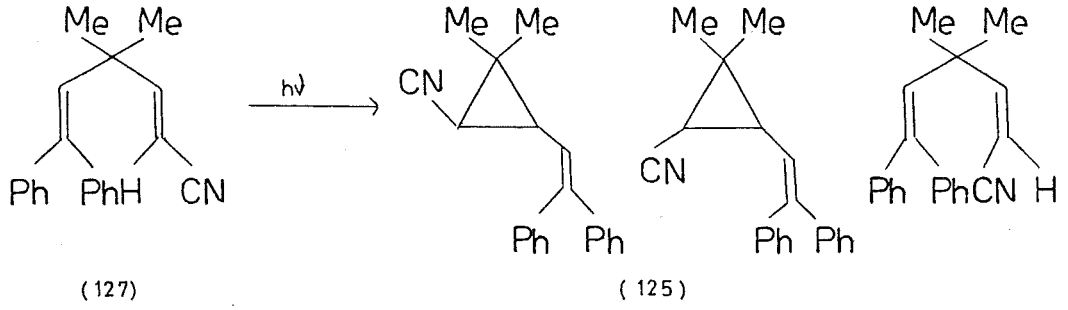
Scheme 49



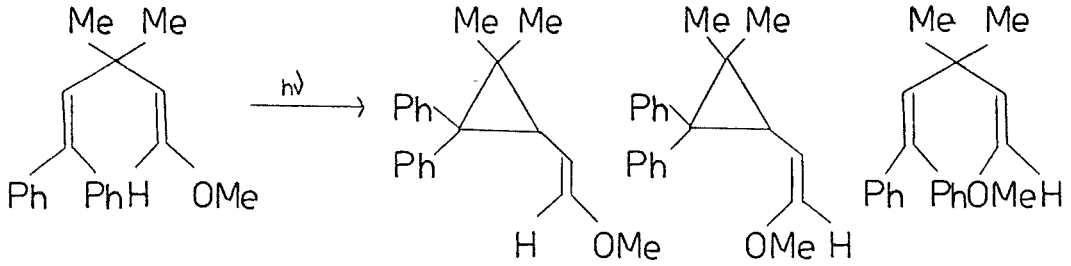
Scheme 50

substituted aryl group is better able to stablise an adjacent odd electron center than unsubstituted phenyl rings. Calculations by Zimmerman show the S_1 excited state(123) was polar and polarisable[73]. Rate inhibition for the methoxy diene(118a) is therefore considered to result from stabilisation of the vertical S_1 excited state(123) slowing down the rate of bridging. Zimmerman has argued that the regioselectivity observed shows that on the opening of the cyclopropyldicarbinyl diradical(124), the carbinyl carbon destined to become the vinyl group becomes less electron rich, leading to stabilisation by electron donating substituents[74].

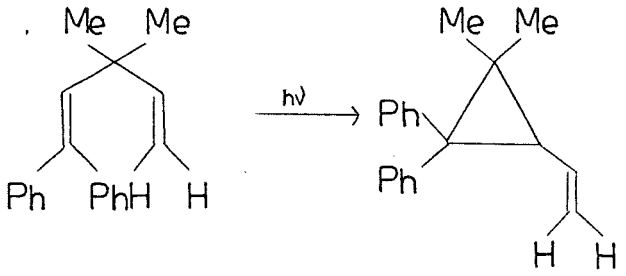
When the polar substituent is bonded directly to the vinyl carbon, rate acceleration relative to the unsubstituted derivative is observed for both electron donating (OMe) and electron withdrawing (CN) groups(Scheme 51)[76]. The regioselectivity observed for the formation of the cyano-substituted cyclopropyl product(125) results from greater stabilisation by the cyano group than the benzhydryl moiety for an electron rich carbinyl carbon of the cyclopropyldicarbinyl diradical(126) and results in cleavage of bond(a) (Scheme 52). The greater stabilisation of the carbinyl radical ($Ph_2C^{\cdot}$) by aryl substitution compared with the $\dot{C}HX$ radical center for X = OMe and H results in cleavage of bond (b). The bridging process involved in the formation of the cyclopropyldicarbinyl diradical species(126) from the S_1 excited state is exothermic and the presence of either electron donating or withdrawing substituents on the resulting radical centers is calculated to increase the exothermicity of the reaction and result in an increase in the rate of the reaction[77]. The 1,4-dienes(127) and (128) rearrange



(127) (125)

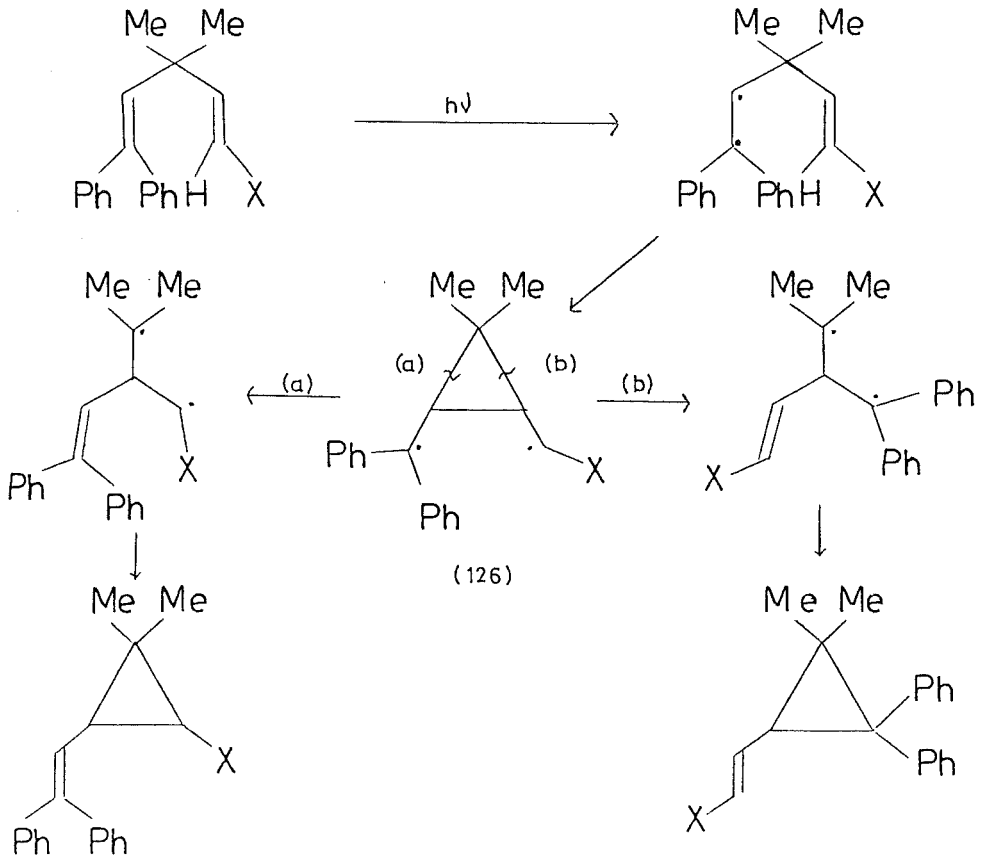


(128)



(129)

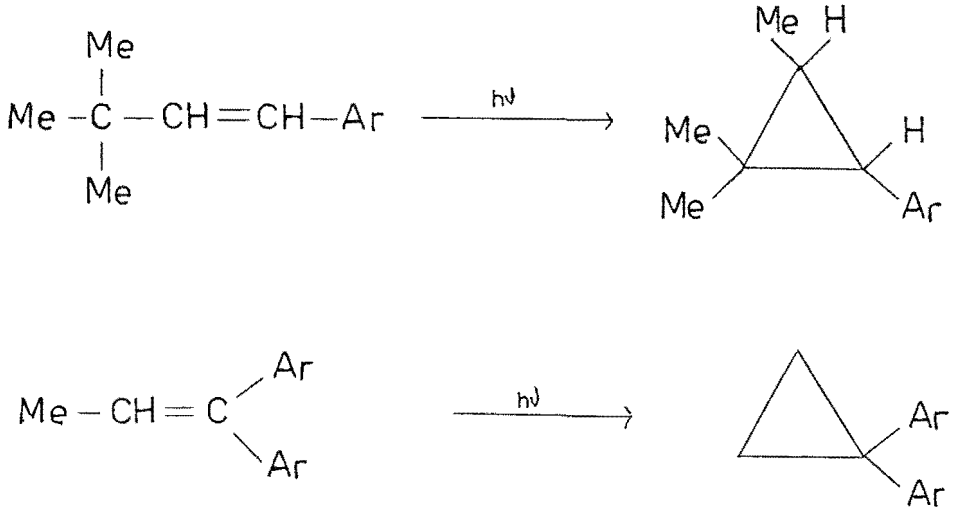
Scheme 51



Scheme 52

to the cyclopropyl products faster than (129)(Scheme 51).

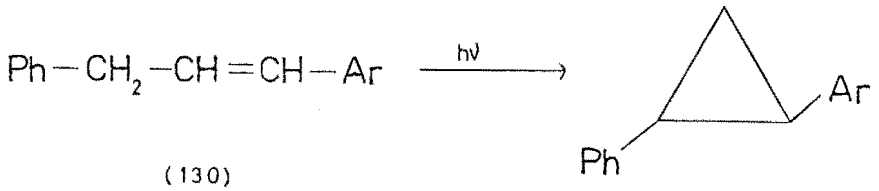
The same rate effects that are observed for the di-vinyl methane system(119), namely rate acceleration by electron withdrawing and rate deceleration by electron donating substituents, are also found for the analogous rearrangement of the π,π^* systems shown in Scheme 53, which undergo 1,2-migrations and give cyclopropane products[78,79].



Scheme 53

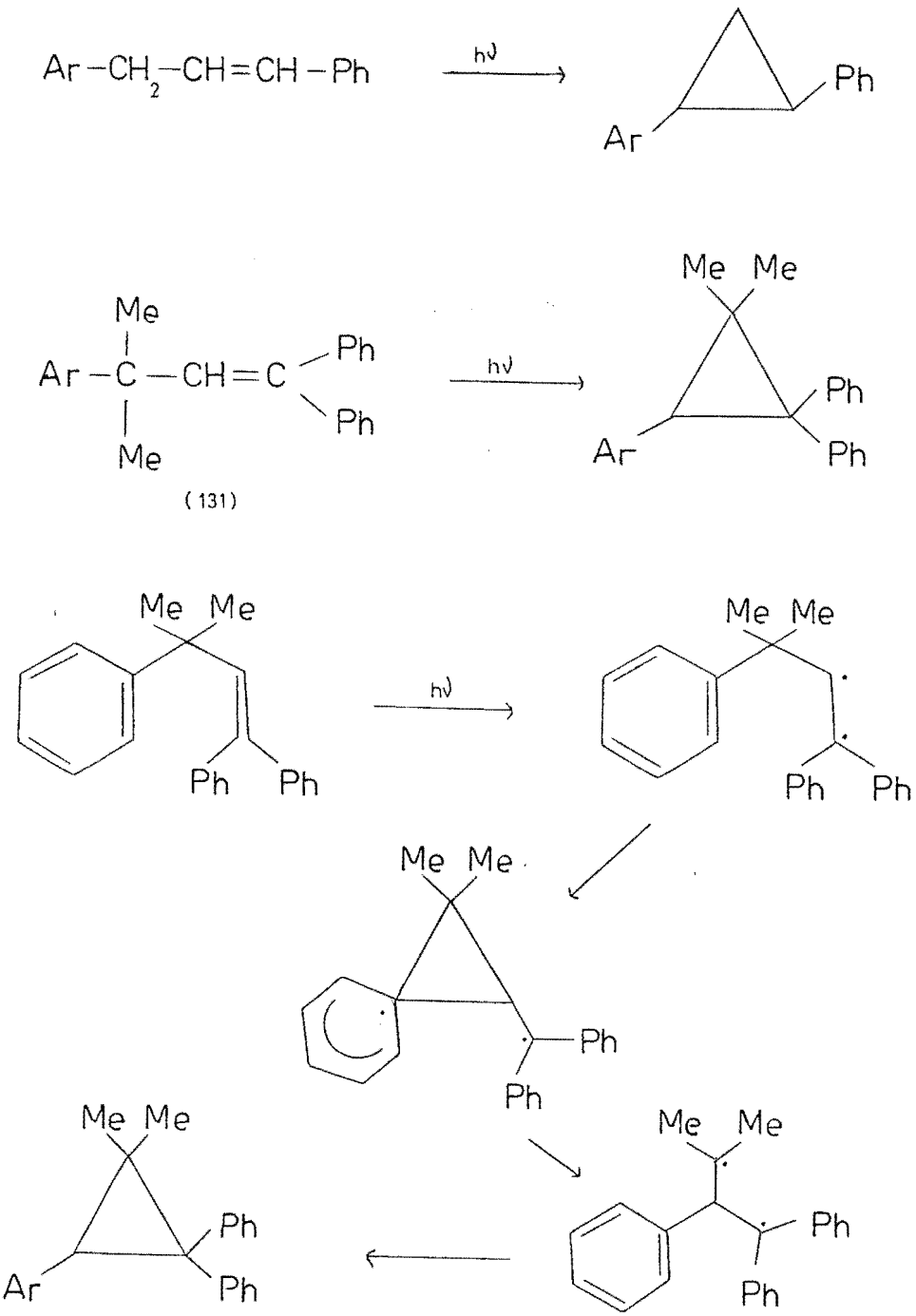
For these latter π,π^* systems, the substituent effect can be explained by the nature of the olefin π,π^* excited states which are electron deficient owing to promotion of one of the bonding electrons to the π^* orbital. Electron donating substituents decrease electron deficiency at the migration terminus and thereby decrease the rate of migration of methyl or hydrogen while electron withdrawing substituents have an opposite effect. Alternatively the substituents could be exerting their effect primarily by raising (OMe) or lowering (CN) the energy of the bonding orbital which is left half filled upon excitation. Lowering the π orbital energy would enhance its interaction with the reactive γC-H bond and increase reactivity.

The effect of substituents on the di-π-methane rearrangement of (130) whereby *para*-cyano substitution accelerates and *para*-methoxy substitution decelerates the rate of cyclopropane formation may similarly be attributed to varying electron density at the migration terminus(C2)[80]. However, the studies on the di-vinyl systems(119) showed that the situation is not simple. Rate deceleration by electron donating substituents for di-vinyl and aryl-vinyl systems may be explained by stabilisation of the vertical S_1 excited state, facilitating intersystem crossing to the T_1 excited state and reducing the rate of bridging. Rate acceleration by the electron withdrawing group (CN) for the aryl-vinyl system(130) is not analogous to the di-vinyl system in that the substituent does not affect the direction of ring opening in the cyclopropyldicarbinyl diradical. An increase in the exothermicity of bridging expected for all substituted aryl-vinyl methane compounds may explain the rate increase.



(130)

The aryl-vinyl methane systems(Scheme 54) undergo an analogous photochemical rearrangement to that described for the di-vinyl methane system(119) but are markedly slower to react since for this process aromaticity is lost along the reaction coordinate(Scheme 54)[58]. The substituent effect

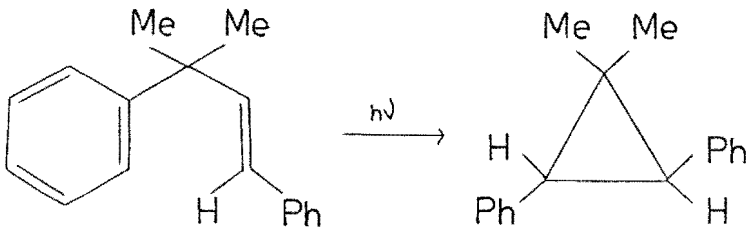


Scheme 54

on the rate of cyclopropane formation observed when the aryl group which is migrating bears the substituent, is less noticeable than when the substituted aryl group is on the excited moiety. The aryl-vinyl methane systems depicted in Scheme 54[80,58] show a rate increase, relative to the unsubstituted phenyl compounds, for both electron donating (OMe) and electron withdrawing (CN) substituents. Zimmerman has calculated that there is relatively little electronic excitation in the migrating aryl group and the substituent effects follow that which would be expected for odd electron stabilisation at the *para* position of the migrating aryl group.

A study of the styryl-vinyl methane system(88) showed that the rate of cyclopropane formation was slower than for the aryl-vinyl methane analogue(131), despite a high quantum efficiency[58]. The rate decrease was suggested to be due to decreased diradical stabilisation in the bridging process as the benzylic center involved is less stabilising than a benzhydryl moiety(Scheme 54).

This present work involves a qualitative study on the effect of aryl substituents on the styryl methane system(88). The absolute reaction rates and quantum efficiencies were not

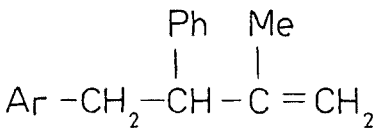


(88)

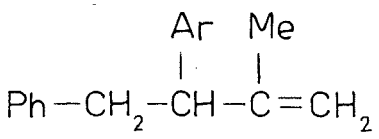
determined but the relative effects of the substituents was determined by examination of the photochemical products formed by reaction of the olefins under standard conditions.

Short term photolyses (0.25hr and 0.5hr) of the substituted *trans*-1-aryl-3-methyl-3-phenylbut-1-enes(88b-g) in *t*-butyl alcohol (Table 2) gave *cis*-1-aryl-3-methyl-3-phenylbut-1-enes(109b-g) and *trans*-1-aryl-3,3-dimethyl-2-phenyl-cyclopropanes(112b-g). The products were identified from their ^{1}Hn.m.r. spectra by comparison with their phenyl analogues.

Longer term photolyses (6hr) of the substituted *trans*-olefins(88b-g) in *t*-butyl alcohol gave *cis*-1-aryl-3-methyl-3-phenylbut-1-enes(109b-g), *trans*-1-aryl-3,3-dimethyl-2-phenyl-cyclopropanes(112b-g) and the terminal alkenes(115, 132) (Table 2). The ^{1}Hn.m.r. and ^{13}Cn.m.r. spectra of the secondary photoproducts did not distinguish between 4-aryl-2-methyl-3-phenylbut-1-enes(115c,d,e,g) and 3-aryl-2-methyl-4-phenylbut-1-enes(132c,d,e,g) and to establish their



(115)



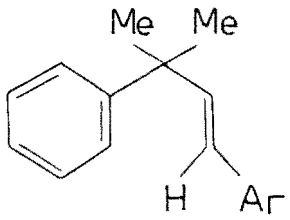
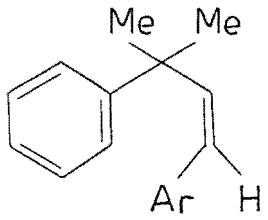
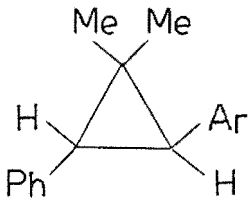
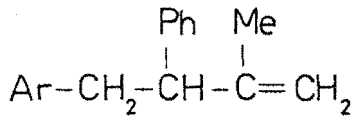
(132)

identity a series of deuterated *trans*-olefins, 1-*d*-1-aryl-3-methyl-3-phenylbut-1-enes(110a,c,d,e) were prepared and their photolyses studied. The deutero-alkenes were prepared by the oxidation of alcohols(97a,c,d,e), followed by reduction with LAD and dehydration with *p*-toluene-sulphonic acid(Scheme 55). As an example, the preparation of the deuterated parent alkene,

TABLE 2

Photolyses of *trans*-1-Aryl-3-methyl-3-phenylbut-1-ene(88) in *t*-BuOH

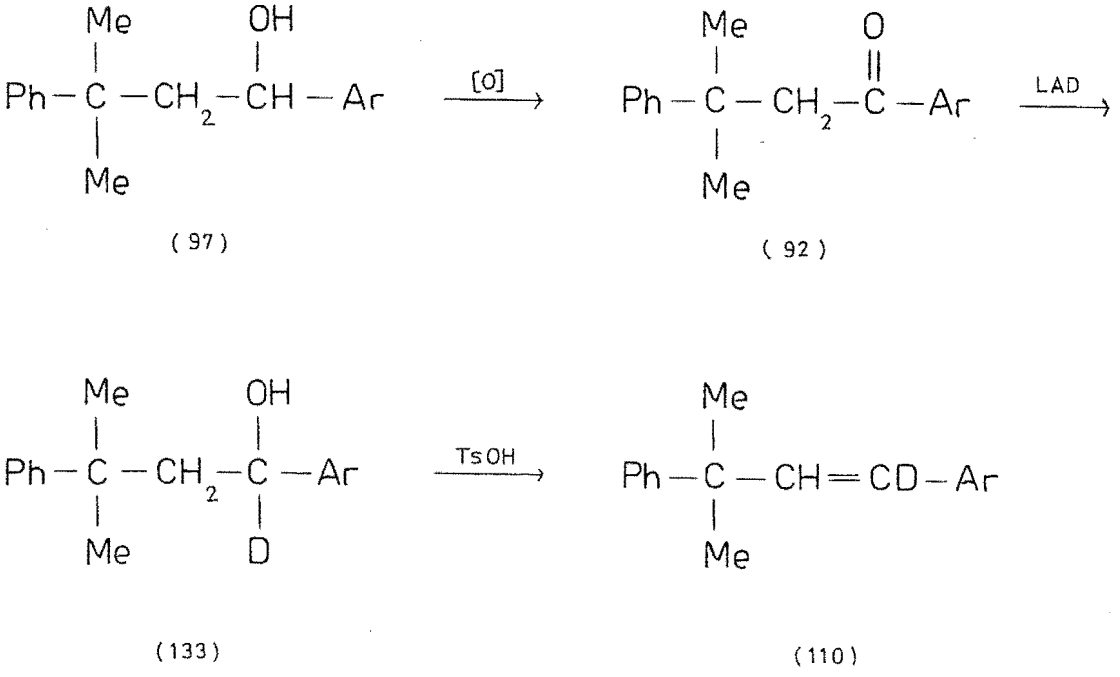
Photoproduct ratio from ^{1}Hn.m.r. spectra of reaction mixture

	(88)			(109)			(112)			(115)		
												
	0.25	0.5	6hr	0.25	0.5	6hr	0.25	0.5	6hr	0.25	0.5	6hr
p-Ph-OMe	75	67	33	25	31	56	-	2	11	-	-	-
p-Ph-Me	75	57	0.5	6	12	0.5	19	31	88	-	-	11
Ph	67	32	-	4	4	-	29	64	71	-	-	29
p-Ph-Cl	74	55	11	22	34	30	4	11	55	-	-	4
m-Ph-Cl	78	55	10	15	32	29	7	13	59	-	-	2
3',4'-Ph-Cl_2	58	40	65*	37	50	32	5	10	3	-	-	-
p-Ph-CN	72	40	6	3	6	6	20	46	8	5	8	80

* Polymerisation of photoproducts is thought to explain anomalous product ratio.

trans-1-*d*-1,3-diphenyl-3-methylbut-1-ene(110a) is described in detail.

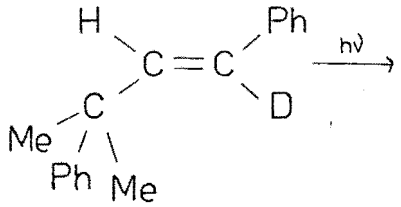
Oxidation of 1,3-diphenyl-3-methylbutan-1-ol(97a) gave 1,3-diphenyl-3-methylbutan-1-one(92a) which was identified by comparison with an authentic sample. Reaction of the ketone(92a) with lithium aluminium deuteride gave 1-*d*-1,3-diphenyl-3-methyl-butan-1-ol(133a) whose ^{1}Hn.m.r. spectrum showed the C2 methylene protons as an AB quartet (δ_H2.01, 1.89, J = 15Hz) since the coupling with the C1D was small. There was a marked simplicity of the methylene signal compared with the ^{1}Hn.m.r. spectrum of the undeuterated alcohol(97a). The loss of the proton signal at δ_H4.4 and the appearance of the 1:1:1 triplet at δ_C72.3 in the ^{13}Cn.m.r. spectrum showed that deuteration at C1 was complete. Dehydration of the deutero-alcohol(133a) with *p*-toluenesulphonic acid under carefully controlled conditions gave the



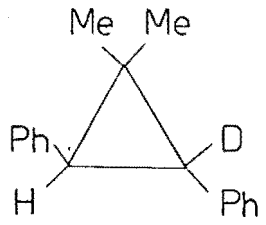
Scheme 55

trans-alkene, 1-*d*-1,3-diphenyl-3-methylbut-1-ene(110a). The ^{1}Hn.m.r. spectrum showed a reduction of the intensity in the vinyl proton region (δ_H6.4) and broadening of the signal to a poorly formed 1:1:1 triplet, J 1.5Hz, by coupling of the C2 hydrogen with ClD. The ^{13}Cn.m.r. spectrum of the deutero-alkene(110a) was identical to that of the undeuterated alkene(88a) except for the loss of the signal at δ_C125.7 which showed that deuteration at C1 was complete and also confirmed the assignment of the alkene carbon signals.

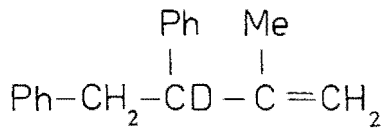
Long term photolysis (6hr) of *trans*-1-*d*-1,3-diphenyl-3-methylbut-1-ene(110a) in benzene, followed by separation of the products on a silver nitrate alumina column, gave *trans*-1-*d*-3,3-dimethyl-1,2-diphenylcyclopropane(134a)(42%) and a 1:1 mixture of 3-*d*-3,4-diphenyl-2-methylbut-1-ene(136a) and 4-*d*-3,4-diphenyl-2-methylbut-1-ene(135a)(43%). The deuterated



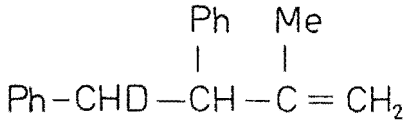
(110a)



(134a)(42%)



(136a)(21.5%)



(135a)(21.5%)

cyclopropane(134a) was identified from its ^{1}Hn.m.r. spectrum which was identical to that of the undeuterated analogue(112a) except for a decrease in the size of the signal due to the cyclopropyl protons at δ_H2.37. The secondary photoproduct olefins(135a,136a) were also identified from comparison of the ^{1}Hn.m.r. and ^{13}Cn.m.r. spectra with those of the

undeuterated analogue(115a). The intensity of the C3(δ_C54.4) and C4(δ_C39.9) signals in the ^{13}Cn.m.r. spectrum were reduced indicating the presence of deuterium at both positions.

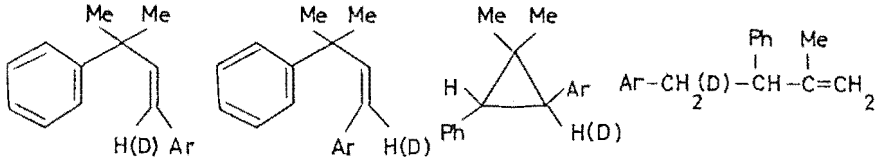
The aryl-substituted deuterated olefins(110c,d,e) were similarly prepared and identified by comparison of their spectral data with those of the undeuterated analogues and of the parent compound(110a). Long term photolyses(6hr) of the *trans*-1-*d*-1-aryl-3-methyl-3-phenylbut-1-enes(110c,d,e) in benzene, followed by separation of the products on silver nitrate alumina columns, gave the *trans*- and *cis*-1-*d*-1-aryl-3-methyl-3-phenylbut-1-enes(110c,d,e ; 137c,d,e), *trans*-1-*d*-1-aryl-3,3-dimethyl-2-phenylcyclopropanes(134c,d,e) and the 4-*d*-4-aryl-2-methyl-3-phenylbut-1-enes(135c,d,e). The yields of these products are given in Table 3. The *cis*- and *trans*-1-*d*-1-aryl-3-methyl-3-phenylbut-1-enes(137c,d,e ; 110c,d,e) and *trans*-1-*d*-1-aryl-3,3-dimethyl-2-phenylcyclopropanes(134c,) d,e) could be identified by comparison of spectral data with those of the undeuterated analogues. The secondary photo-products, 4-*d*-4-aryl-2-methyl-3-phenylbut-1-enes(135c,d,e) could be similarly identified. The replacement of the C4 signal (c.δ_C39) in their ^{13}Cn.m.r. spectra by a 1:1:1 triplet indicated that deuterium was present only at C4.

The formation of the terminal olefins in the photolyses of (134c,d,e) involves C1-C3 cyclopropyl bond cleavage irrespective of the substituent on the phenyl ring(Scheme 56). The regioselectivity appears to be governed by the ability of the aryl group to stabilise the benzylic radicals. A concerted $[\sigma_s^2 + \sigma_s^2]$ mechanism for cyclopropyl ring cleavage and 1,4-hydrogen migration is unlikely to exhibit such a substituent effect and therefore it is considered that reaction involves formation of a diradical species with hydrogen transfer being faster than C-C bond rotation.

TABLE 3

Photolyses of *trans*-1-aryl-3-methyl-3-phenylbut-1-enes(88,110) in benzene[a]

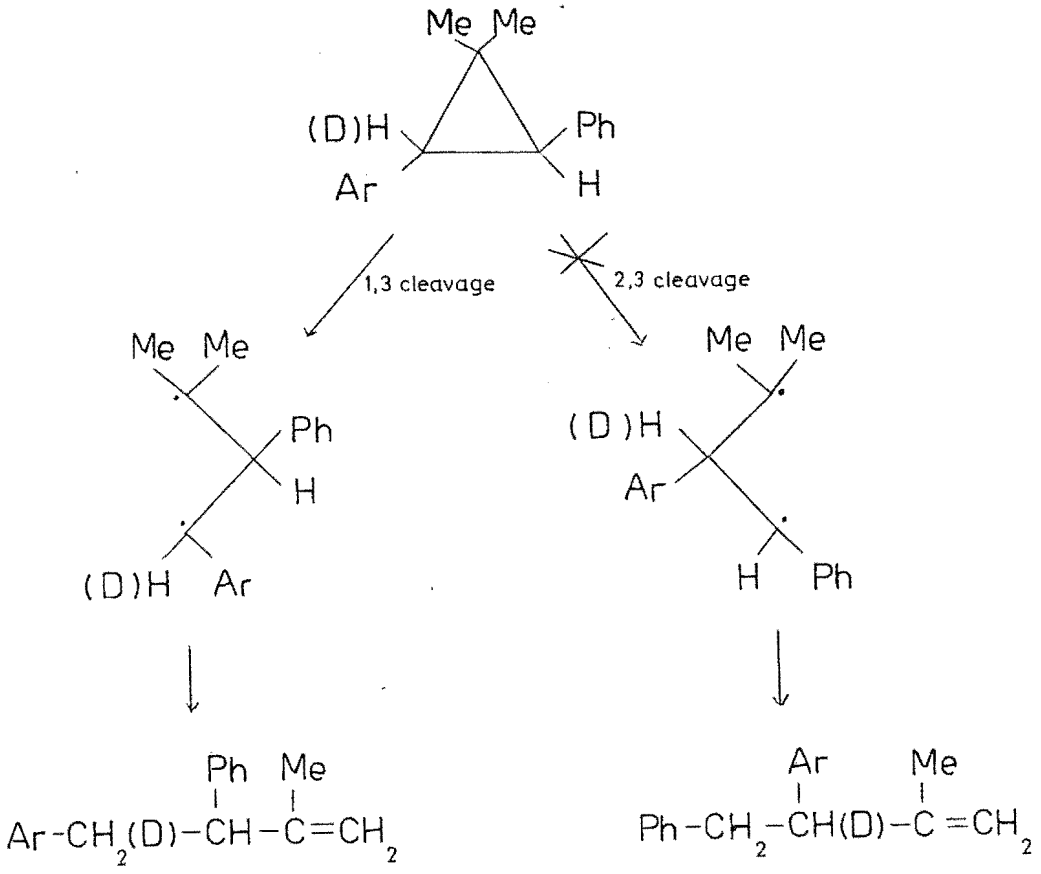
Photoproduct percentage isolated by column chromotography.



	88(110)	109(137)	112(134)	115(135)
p-Ph-OMe	39	28	5	-
p-Ph-Me	5(-)	2(-)	67(64)	22(12)
Ph	-(-)	-(-)	49(42)	32(43)
p-Ph-Cl	14(14)	7(21)	38(41)	13(12)
m-Ph-Cl	14(7)	11(11)	30(23)	5(16)
3',4'Ph-Cl_2	38	29	6	-
p-Ph-CN	32[b]	4	34	5

(a) Photolysed for 6hr.

(b) Cyano-substituted alkene photolysed 1hr.

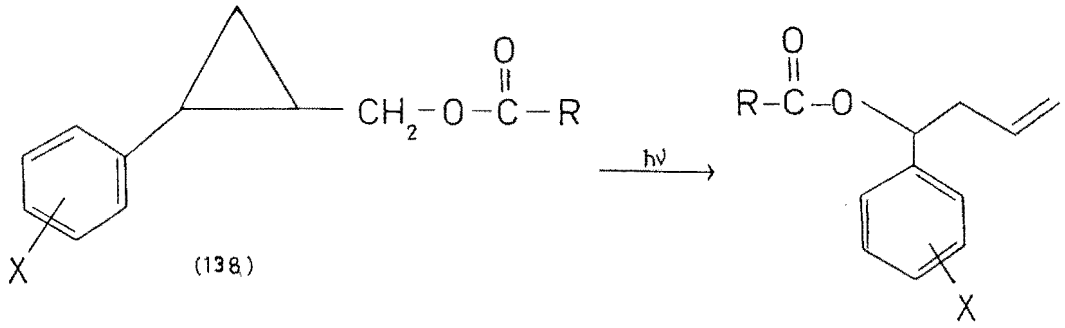


Scheme 56

The ultra-violet spectra of the substituted *trans*-1-aryl-3, 3-dimethyl-2-phenylcyclopropanes(112a-g) show conjugation in the $\pi - \pi^*$ region, with the aryl and the three-membered ring. Excitation of the cyclopropyl aryl moiety on irradiation results in homolysis of the weakest cyclopropyl bond - the bond flanked by the substituted aryl group is most capable of stabilising the resulting odd electron center.

Formation of the secondary photoproduct was observed for Ar = Ph, *p* - PhMe, *p* - PhCl and *m* - PhCl only after long term irradiation of the *trans*-alkenes(88a,c,d,e). 4-(4' - Cyanophenyl)-2-methyl-3-phenylbut-1-ene(115g) was observed during the short term irradiation of the *trans*-alkene(88g) which shows that the cyano-substituted cyclopropane(112g) is particularly photolabile relative to the other substituted cyclopropanes (Ar = Ph, PhMe, PhCl). Hixson and his

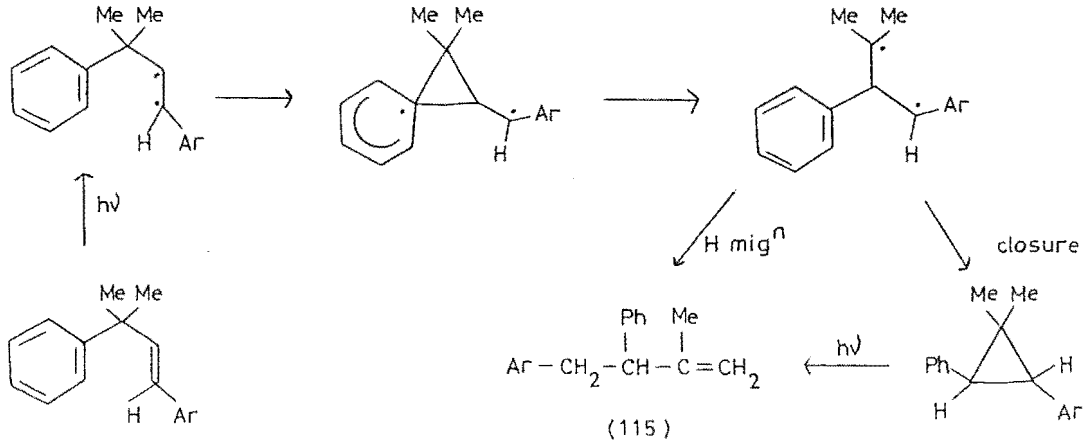
coworkers[81] have shown by ultra-violet studies of aryl-substituted cyclopropanes(138) that the conjugative interaction between the aryl and the cyclopropane ring is best when there is an electron withdrawing group on the aromatic ring. They explained the reaction rate increase observed for the electron withdrawing substituents (CN) by the more substantial



(138)

cyclopropane bond weakening expected on excitation of the molecule due to this conjugation. Electron donating substitutents (OMe) on the aryl group lessen the conjugation between the cyclopropyl and aromatic rings and lessen the cyclopropane bond weakening on excitation. This is reflected in the retardation of the rate of rearrangement observed for these substituents.

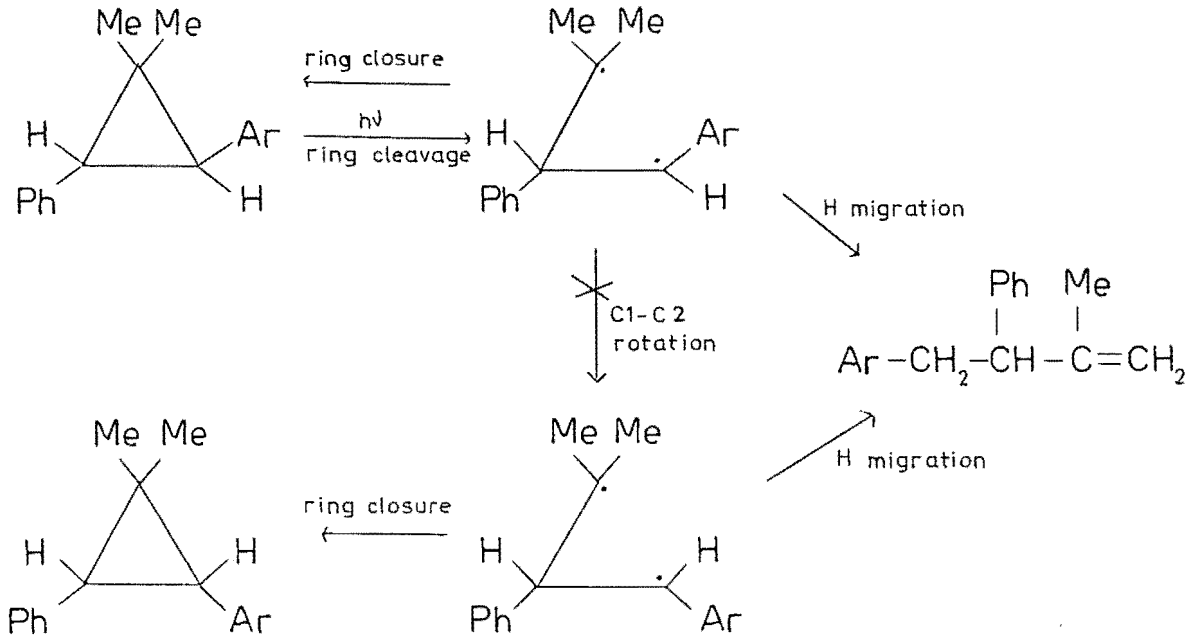
From Table 2 it can be seen that only for the photolysis of *trans*-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(88g) could the terminal alkene(115g) be formed as a primary photoproduct(Scheme 57). For all other substituents the



(88) (115) (112)

Scheme 57

build-up of cyclopropane product before the decay to the secondary photoproduct indicates that for Ar = Ph, *p*-PhMe, *p*-PhCl and *m*-PhCl, closure of the biradical intermediate is faster than hydrogen migration. Failure to detect *cis*-cyclopropane derivatives indicates that on photo-induced ring cleavage of the cyclopropane ring, hydrogen migration and ring closure are faster than rotation about the C1-C2 bond of any intermediate biradical(Scheme 58).

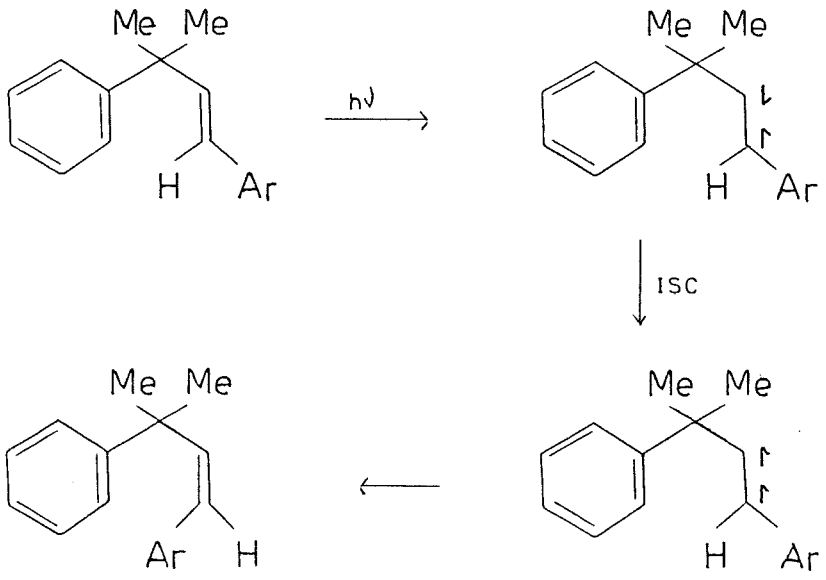


Scheme 58

The effect of the substituents on the C1 phenyl ring of *trans*-1-aryl-3-methyl-3-phenylbut-1-enes(88) on the extent of cyclopropane formation was determined for both the short and long term photolyses (Table 2). The proportions of 1-aryl-3,3-dimethyl-2-phenylcyclopropanes(112) and secondary photoproducts(115) formed over a standard period in time gives some indication of the relative reaction rates. The yield of the cyclopropane and secondary photoproduct is highest for Ar = Ph > *p*-PhMe ≈ *p*-PhCN and lowest for Ar = *p*-PhOMe.

Zimmerman has rationalised the decrease in the rate of cyclopropane formation observed for Ar = *p*-PhOMe and *p*-$PhNMe_2$, in the divinyl methane system(119) by stabilisation of the S_1 vertical excited state(123) by the substituents[73]. The lower S_1 excited state energy may increase the amount of intersystem crossing to T_1, resulting in *cis-trans* isomerisation which can, of course, not be observed in this series of compounds.

The small degree of cyclopropane formation, on irradiation of *para*-methoxy and chloro-substituted styryl-vinyl methane compounds(88b, d, e, f) can be explained if the substituents lower the energy of S_1. The formation of relatively large proportions of *cis*-alkene for the *p*-methoxy and chloro-substituted compounds(88) is consistent with a lower S_1 excited state enabling intersystem crossing to the T_1 excited state which undergoes *trans-cis* isomerisation and from which cyclopropane formation does not occur(Scheme 59).



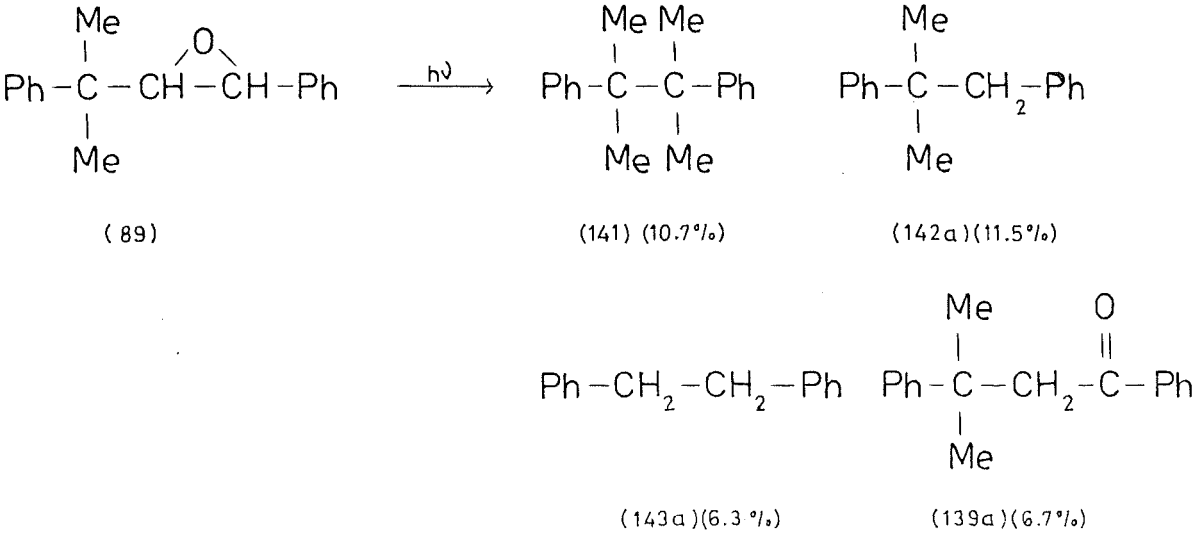
Scheme 59

The effect that the Cl-aryl substituents have on the efficiency of cyclopropane formation in the styryl-vinyl system(88) may also be rationalised by analogy with the simple π,π^* systems(Scheme 53). For these systems the reaction is said to be slower for compounds for which the aryl substituent increases the electron density at the migration terminus (C2) and that rate acceleration is induced by a decrease in electron density at C2, affected by electron withdrawing substituents on the aryl ring[78].

Photolysis of *trans*-1-Aryl-1,2-epoxy-3-methyl-3-phenylbutanes(89)

In the previous section it was observed that irradiation of the styryl-vinyl systems, *trans*-1-aryl-3-methyl-3-phenylbut-1-enes(88a-g), results in a rearrangement analogous to the di-π-methane rearrangement with formation of cyclopropane products(112a-g). In order to determine the effect that replacement of the vinyl moiety by an epoxide ring has on the photorearrangement of this system a series of *trans*-1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes(89a-e) were prepared by epoxidation of the precursor alkenes(88) with *m*-chloroperbenzoic acid. The parent epoxide, *trans*-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a) was irradiated in light petroleum solution for 8hr while the reaction was monitored by g.l.c. and t.l.c. The ^{1}Hn.m.r. spectrum of the reaction residue showed the presence of 1,3-diphenyl-3-methylbutan-2-one(139a) and 2,3-diphenyl-3-methylbutanal(140a) in a ratio of c.3:1 as determined by integration of the signals at δ_H9.78 and δ_H3.48. Chromotography of the reaction product gave 2,3-dimethyl-2,3-diphenylbutane(141)(10.7%), 1,2-diphenyl-2-methylpropane(142a)(11.5%), 1,2-diphenylethane(143a)(6.3%), unreacted epoxide(89a)(10.6%) and 1,3-diphenyl-3-methylbutan-2-one(139a)(6.7%).

Irradiation of the epoxide(89a) in benzene solution



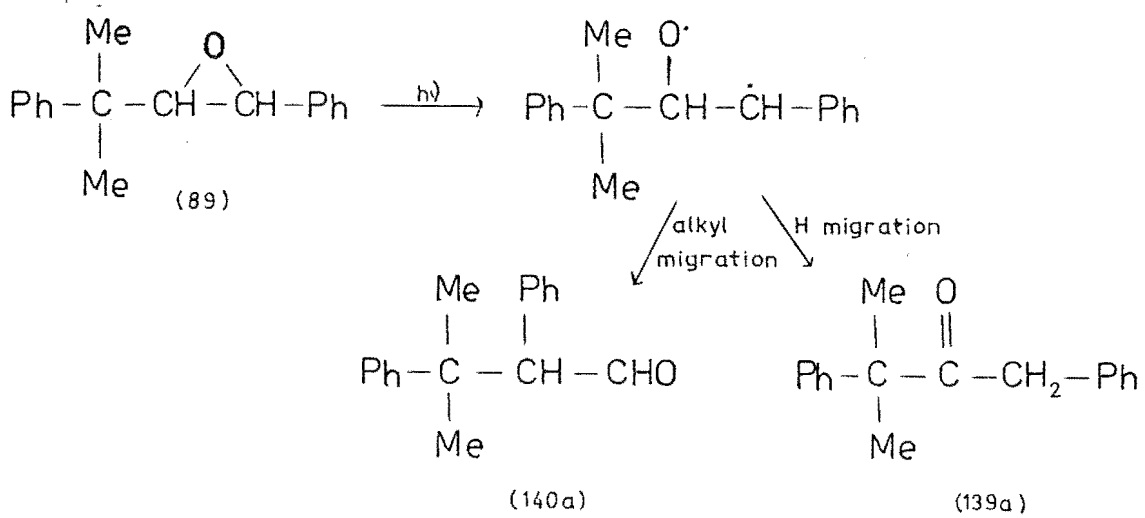
(89) (141) (10.7%) (142a)(11.5%)

(143a)(6.3%) (139a)(6.7%)

enabled the isolation of the same products in similar yields: (141)(8.8%), (142a)(10.8%), (143a)(8.8%), (89a)(27.3%) and (139a)(9.5%).

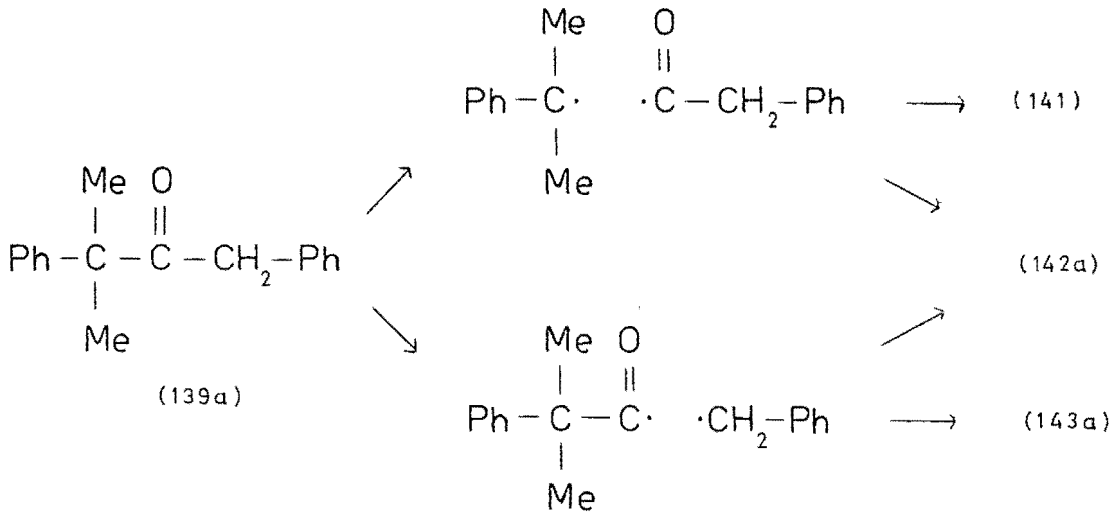
2,3-Dimethyl-2,3-diphenylbutane(141)[61] was identified from its ^{1}Hn.m.r. spectrum which showed the resonances for methyl protons at δ_H1.28 and for the aromatic protons at δ_H7.08. The ^{1}Hn.m.r. spectrum of 1,2-diphenyl-2-methylpropane (142a)[82] showed the signals for the methyl protons at δ_H1.30, the methylene protons at δ_H2.85 and the aromatic protons at δ_H7.15. The ^{1}Hn.m.r. spectrum of 1,2-diphenylethane(143a)[83] revealed absorptions for the methylene protons at δ_H2.90 and for the aromatic protons at δ_H7.12. 1,3-Diphenyl-3-methylbutan-2-one(139a)[84] was identified by comparison of its spectral data with those obtained for the same ketone formed by reaction of BF_3-etherate and epoxide(89a) (see p.135). The aldehyde, 2,3-diphenyl-3-methylbutanal(140a) could not be isolated by column chromotography but was identified in the reaction residue by comparison with the spectral data obtained for that aldehyde on BF_3-etherate reaction with the epoxide (89a) (see p.117).

The ketone(139a) is formed by C1-O bond cleavage followed by hydrogen migration(Scheme 59). 1,2-Hydrogen



Scheme 59

migrations are rare and are symmetry forbidden in ground state diradicals[32]. The hydrocarbons are secondary photoproducts formed by α-cleavage of the ketone(139a). This was shown by a separate experiment in which irradiation of the ketone(139a) gave a mixture of the hydrocarbons as the only products. Both C1-C2 and C2-C3 bonds break on photolysis resulting in the formation of two hydrocarbon radicals and two ketyl radicals. The hydrocarbon radicals recombine to give the three hydrocarbon products observed. Recombination of the ketyl radicals would produce photolabile products which are not observed in the product mixture(Scheme 60).



Scheme 60

The aldehyde, 2,3-diphenyl-3-methylbutanal(140a) can be formed by C1-O bond cleavage followed by alkyl migration or by C2-O bond cleavage followed by phenyl migration. The absence of 1,3-diphenyl-3-methylbutan-1-one(92a) and its photoproducts imply that C2-O bond cleavage is at most a minor reaction process and it can probably be assumed that the aldehyde formed is by C1-O bond cleavage and alkyl migration (Scheme 59).

The substituted epoxides(89b-e) were irradiated in benzene solution and the products isolated by column

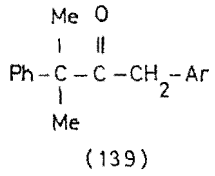
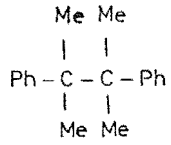
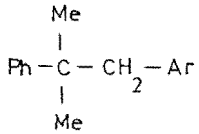
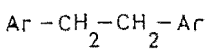
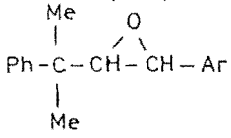
chromotography. These were identified as 2,3-dimethyl-2, 3-diphenylbutane(141), the 1-aryl-2-methyl-2-phenylpropanes (142b-e), the 1,2-diarylethanes(143b-e), the 1-aryl-3-methyl-3-phenylbutan-2-ones(139b-e) and unreacted epoxides(89b-e). The percentage yields of the products isolated from each epoxide's reaction are given in Table 4. The ^{1}Hn.m.r. spectra of the crude reaction products showed that the 2-aryl-3-methyl-3-phenylbutanals(140b-e) and ketones(139b-e) were formed from each substituted epoxide in the ratio of c.1:3. For the *meta*-chloro substituted epoxide(89e) however, no aldehyde was detected. Loss of polymeric and unstable photoproducts occurs on column chromotography and results in low yields of isolated products.

As a result of these studies, it is seen that the 1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes(89a-e) do not undergo analogous photorearrangements to those observed for the precursor alkenes(88a-e) on irradiation. Rather, they follow a pathway characteristic of the epoxide moiety, that is, C-O bond cleavage followed by group migration. The ketones(139a-e) formed are also photolabile and undergo cleavage of the C-C bonds adjacent to the carbonyl group in the typical Norrish Type I rearrangement.

Table 4

Photolyses of *trans*-1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes(89)

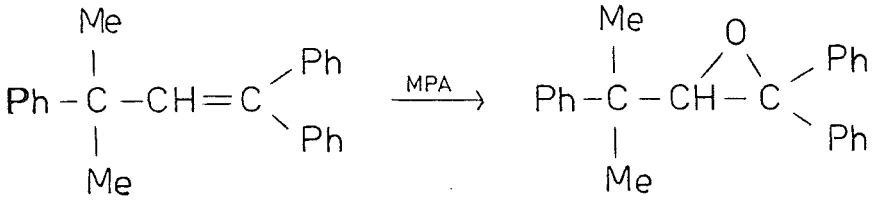
Percentage weight isolated.

Ar	Ph	*p*-PhOMe	*p*-PhMe	*p*-PhCl	*m*-PhCl
 (139)	9.5	6	13.6	3.3	13
 (141)	8.8	12	8.6	8.2	12
 (142)	10.8	11	8.9	2.2	5.3
 (143)	8.8	9.3	7.0	2.5	5.3
 (89)	27	9	25	18	16

Preparation and Photolysis of 1,2-Epoxy-3-methyl-1,1,3-triphenylbutane(144) and 2,3-Diphenyl-1,2-epoxy-3-methylbutane(149)

In a further attempt to observe interaction between the epoxide moiety and a site of unsaturation in the form of an aromatic ring, epoxides (144) and (149) were prepared. The former epoxide (144) was expected to be more reactive than the previous epoxide series(89) and could be expected to show photoreactions typical of the more reactive epoxide systems which undergo C-C bond cleavage in addition to C-O bond cleavage.

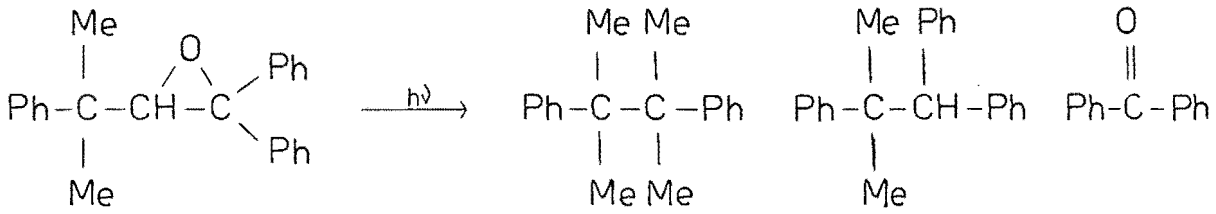
The synthesis of 3-methyl-1,1,3-triphenylbut-1-ene(131) has been reported by Zimmerman[58] and this compound was prepared following his outline. Reaction of the alkene(131)



(131) (144)

with an ethereal solution of monoperphthalic acid gave 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144). The i.r. spectrum of the epoxide(144) showed a C-O-C stretch(ν 1250 cm^{-1}) and the ^{1}Hn.m.r. spectrum showed the presence of signals from two methyl groups(δ_H1.07, 1.12), from the single epoxide proton(δ_H3.50) and a multiplet due to three phenyl rings (δ_H7.30, Wh/2 6Hz). The ^{13}Cn.m.r. spectrum showed peaks arising from two methyl groups(δ_C23.8, 28.1), from the C2 carbon(δ_C74.0), from two quaternary carbons(C1, δ_C66.5; C3, δ_C39.2) and twelve peaks due to three phenyl rings.

The epoxide(144) was irradiated in benzene and light petroleum solutions and the products isolated by column chromotography were 2,3-dimethyl-2,3-diphenylbutane(141)(4.7%, 3.9% respectively), 2-methyl-1,1,2-triphenylpropane(145)(9.2%, 1.9% respectively), benzophenone(46)(16%,5.4% respectively) and unreacted epoxide(144)(26%, 40% respectively).

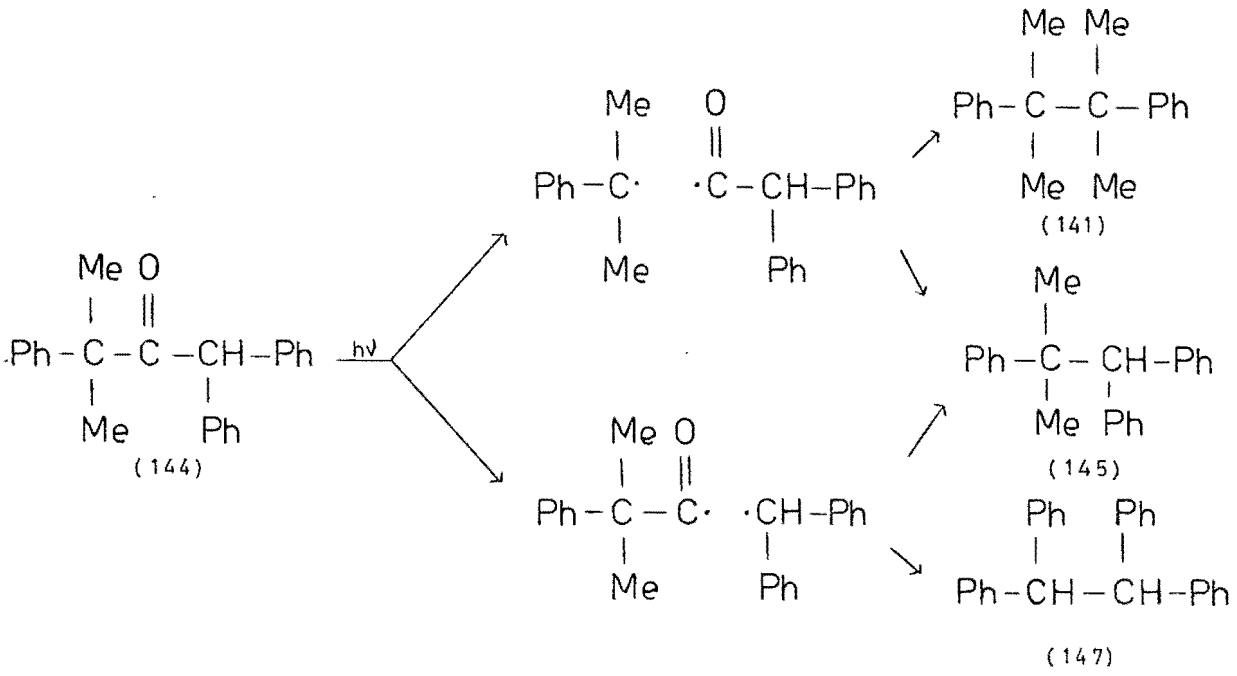


(144) (141) (145) (46)

2,3-Dimethyl-2,3-diphenylbutane(141) and benzophenone(46) were identified by comparison of their spectra with those of authentic samples. The ^{1}Hn.m.r. spectrum of 2-methyl-1,1,2-triphenylpropane(145)[82] showed signals for the methyl protons (δ_H1.40), for the methine proton (δ_H4.13) and for the aromatic protons(δ_H7.12, Wh/2 3Hz).

The hydrocarbons (141) and (145) are secondary photo-products resulting from irradiation of the ketone, 3-methyl-1,1,3-triphenylbutan-2-one(146). Cleavage of both the C1-C2 and C2-C3 bonds results in the formation of hydrocarbon and ketyl radicals. Recombination of the hydrocarbon radicals gives three products (140),(145) and (147)(Scheme 61). 1,1,2,2-tetraphenylethane(147) was not detected in this photolysis reaction and it has been reported that this compound is photolabile[85]. The intermediate ketone(146) could not be detected in the photoreaction mixture.

Irradiation of the epoxide(144) also resulted in

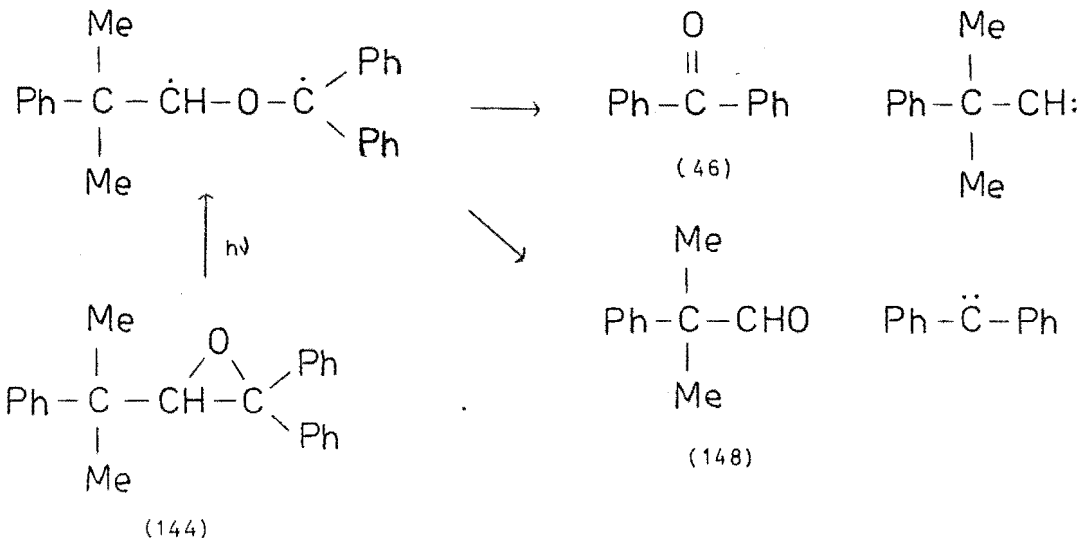


Scheme 61

C-C bond cleavage of the epoxide ring(Scheme 62) in a reaction analogous to that observed for phenyl oxiranes by Griffin(Scheme 7)[20]. Cleavage of the C-O bond leads to formation of carbonyl products and carbenes.

The aldehyde(148) was not detected in the reaction mixture. Polymeric and unstable photoproducts were lost on column chromotography resulting in a low yield of isolated product.

The two previous epoxide systems studied, (89) and (144), are such that Cl-O bond cleavage is expected on



Scheme 62

irradiation. By way of contrast, 2,3-diphenyl-1,2-epoxy-3-methylbutane(149) would be expected to undergo C2-O bond cleavage on irradiation leading to some different types of photorearrangements.

The epoxide(149) was therefore prepared by the reaction of 2,3-diphenyl-3-methylbut-1-ene(150)[86] with *m*-chloroperbenzoic acid. The ^{1}Hn.m.r. spectrum of the

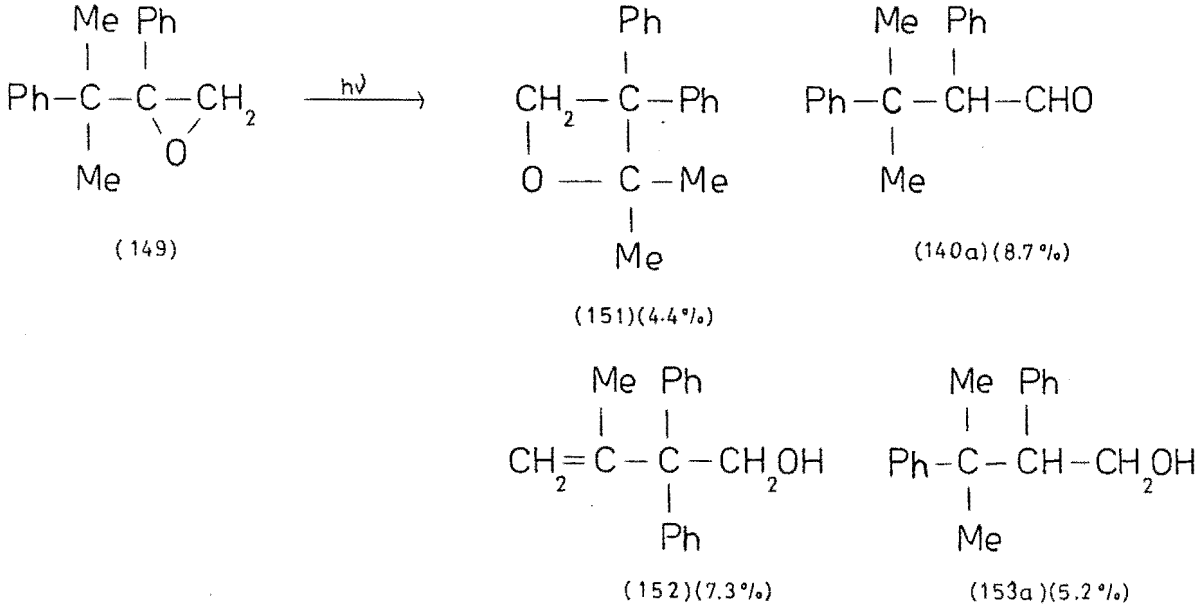
(150) (149)

epoxide(149) showed the methyl protons as a single peak (δ_H1.33), the methylene protons as an AB quartet(δ_H2.64, 3.14, J 5Hz) and the aromatic protons as a broad multiplet centered at δ_H7.13(Wh/2 17Hz). The ^{13}Cn.m.r. spectrum showed resonances for the methyl carbons(δ_C24.2, 25.2) and the aromatic carbons(C2: δ_C138.8, 126.7, 128.2, 126.0; C3: δ_C145.5, 127.2, 128.2, 126.6). The epoxide carbons gave peaks at δ_C50.8(C1) and δ_C66.0(C2) and C3 at δ_C40.7.

Irradiation of the epoxide(149) in benzene solution gave no detectable reaction after 8hr. Addition of benzophenone to the benzene solution and irradiation for 7hr also showed very little reaction. 2,3-Diphenyl-3-methylbutanal(140a) was detected by ^{1}Hn.m.r. spectroscopy in the reaction mixture(δ_H3.72, J 3Hz, H2; δ_H9.79, J 3Hz, H1).

Irradiation of the epoxide(149) in acetone for 8hr gave 2,2-dimethyl-3,3-diphenyloxetane(151)(4.4%), 2,3-diphenyl-3-methylbutanal(140a)(8.7%), 3,3-diphenyl-4-hydroxy-2-methylbut-1-ene(152)(7.3%), 2,3-diphenyl-3-methylbutan-1-ol(153a)(5.2%)

and unreacted epoxide(149)(44%) which were isolated by chromotography.



(149)

(151)(4.4%)

(140a)(8.7%)

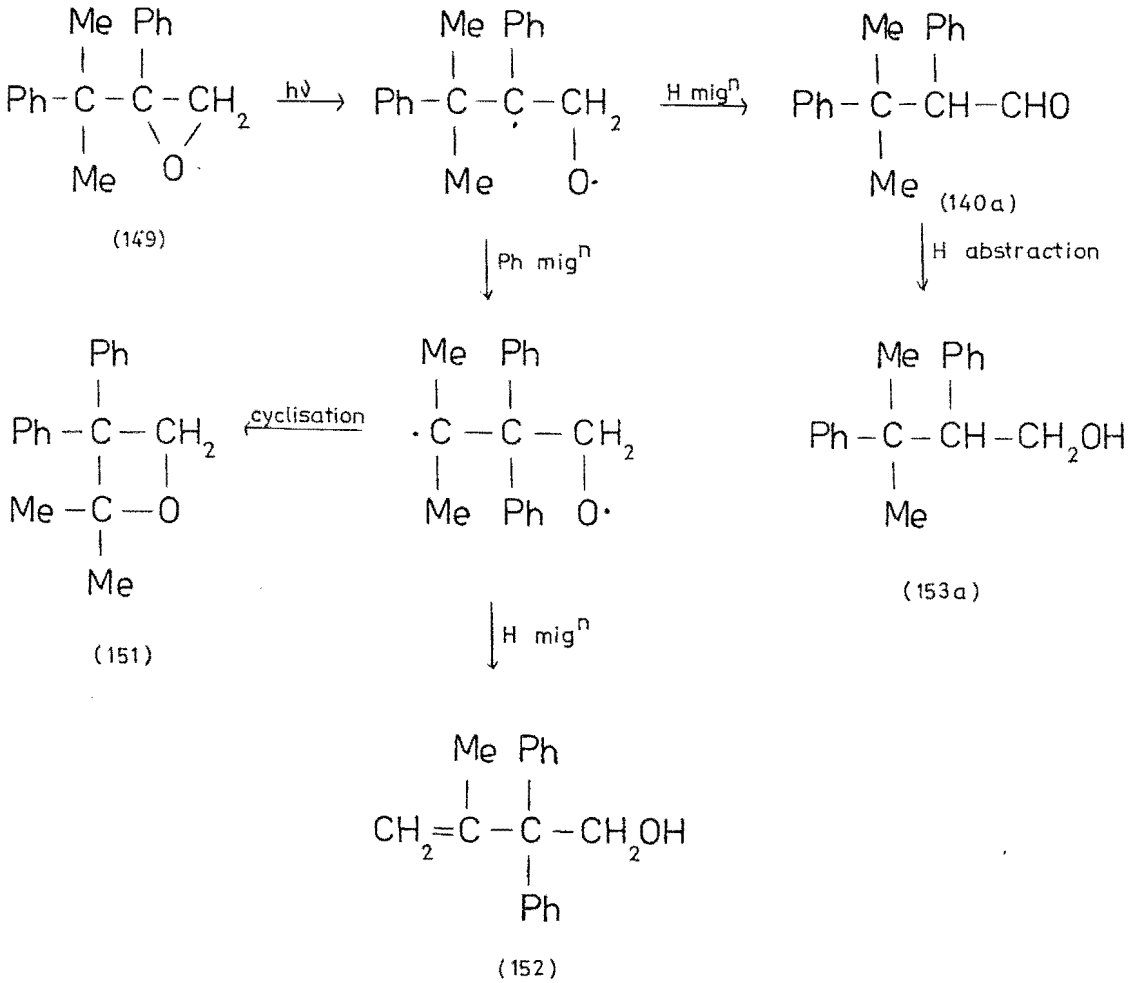
(152)(7.3%)

(153a)(5.2%)

The ^{1}Hn.m.r. spectrum of the oxetane(151) showed the presence of peaks for methyl protons(δ_H1.33), for methylene protons(δ_H5.03) and for aromatic protons(δ_H7.17). The ^{13}Cn.m.r. spectrum showed resonances from the methyl carbons (δ_C27.4) and from the aromatic carbons(δ_C142.8, 128.0, 128.1, 126.5). Two quaternary carbons gave peaks at δ_C91.0 and δ_C58.4 and the methylene carbon signal appeared at δ_C76.9. The ^{1}Hn.m.r. spectrum of 3,3-diphenyl-4-hydroxy-2-methylbut-1-ene(152) showed the methyl signal at δ_H1.68 and the hydroxyl resonance(δ_H1.48) which disappeared on addition of D_2O. The methylene protons appeared as a singlet at δ_H4.36, the aromatic proton signal at δ_H7.26 and the vinyl protons gave peaks at δ_H4.85 and δ_H5.16. The infrared spectrum showed the presence of the hydroxy group(ν 3580 cm^{-1}) and the terminal alkene(ν 1635, 910 cm^{-1}). The ^{13}Cn.m.r. spectrum showed the methyl signal(δ_C21.5) and the aromatic carbon peaks(δ_C143.0, 129.3, 128.1, 126.6). The terminal vinyl carbon resonance appeared at δ_C116.1, the methylene carbon

peak at δ_C68.5 and the quarternary carbon signal at δ_C59.9. 2,3-Diphenyl-3-methylbutanal(140a) and 2,3-diphenyl-3-methylbutan-1-ol(153a) were identified by comparison with authentic samples.

The mechanistic scheme proposed for the photorearrangement of the epoxide(149) is outlined in Scheme 63. On irradiation the C2-O bond breaks and hydrogen migration from C1 competes with phenyl migration from C3. It is notable that only phenyl migration is observed from C3, not methyl migration, and this is contrary to the preference for alkyl



Scheme 63

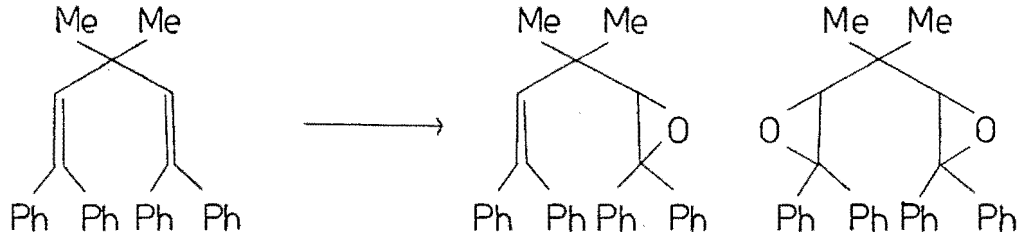
migration observed in the photolysis of the β,γ-epoxy-ketone (59)[28]. Hydrogen migration from C1 results in the formation of the aldehyde(140a) which can undergo photoreduction to the primary alcohol(153a). Photoreductions of carbonyl compounds to give alcohols occur readily where hydrogen abstractions involve the carbonyl moiety in the triplet excited state. Phenyl migration from C3 results in the formation of a 1,4-diradical intermediate. 1,5-Hydrogen migration to give the alcohol(152) is analogous to γ-hydrogen abstraction observed during the photolysis of the β,γ-epoxy ketones(Scheme 18, 19)[40,41]. Cyclisation of the 1,4-diradical intermediate to form the oxetane(151) is analogous to cyclobutanol formation on irradiation of acyclic β,γ-epoxy ketones(Scheme 18, 19)[40,41]. Formation of cyclic ethers is also observed on the irradiation of cyclic β,γ-epoxy ketones(Scheme 15)[38] and indene oxide Scheme 14)[33].

Preparation and Photolysis of β,γ-Unsaturated Epoxides

In order to study the possible interaction between the epoxide moiety and a site of unsaturation in the form of a vinyl bond on irradiation, the following β,γ-unsaturated epoxides, 3,3-dimethyl-4,5-epoxy-1,1,5,5-tetraphenylpent-1-ene(154), 3,3-dimethyl-4,5-epoxy-1,5,5-triphenylpent-1-ene(161), 3,3-dimethyl-4,5-epoxy-1,1,5-triphenylpent-1-ene(160), 1,1-diphenyl-4,5-epoxy-3,3,5-trimethylhex-1-ene(163), 4,5-epoxy-1-phenyl-3,3,5-trimethylhex-1-ene(166), 3,3-dimethyl-4,5-epoxy-2,5,5-triphenylpent-1-ene(169) and 3,3-dimethyl-4,5-epoxy-1,1,4-triphenylpent-1-ene(168) were prepared and their photolyses studied.

(a) 3,3-Dimethyl-4,5-epoxy-1,1,5,5-tetraphenylpent-1-ene(154)

3,3-Dimethyl-1,1,5,5-tetraphenylpenta-1,4-diene(3) was prepared by the method used by Zimmerman[3] and was reacted with monoperphthalic acid to give 3,3-dimethyl-4,5-epoxy-1,1,5,5-tetraphenylpent-1-ene(154)(45%) and 1,2-4,5-diepoxy-3,3-dimethyl-1,1,5,5-tetraphenylpentane(155)(15%) which were readily separated by chromotography. The mono-epoxide(154) was identified from its ^{1}Hn.m.r. spectrum which showed signals from two methyl signals(δ_H0.77, 0.90), from an epoxide proton (δ_H3.07), from a vinyl proton(δ_H5.85) and from aromatic protons(δ_H7.25). The infrared spectrum showed the presence of the epoxide moiety(ν 1250 cm^{-1}) and the vinyl group (ν 760 cm^{-1}). The ^{13}Cn.m.r. spectrum showed peaks for the methyl carbons(δ_C27.0), for the quaternary C3(δ_C38.0), for the



(3) (154) (155)

epoxide carbons(C4, δ_C75.1; C5, δ_C66.2), for the vinyl carbons (C1, δ_C139.7; C2, δ_C134.3) and for the phenyl rings.

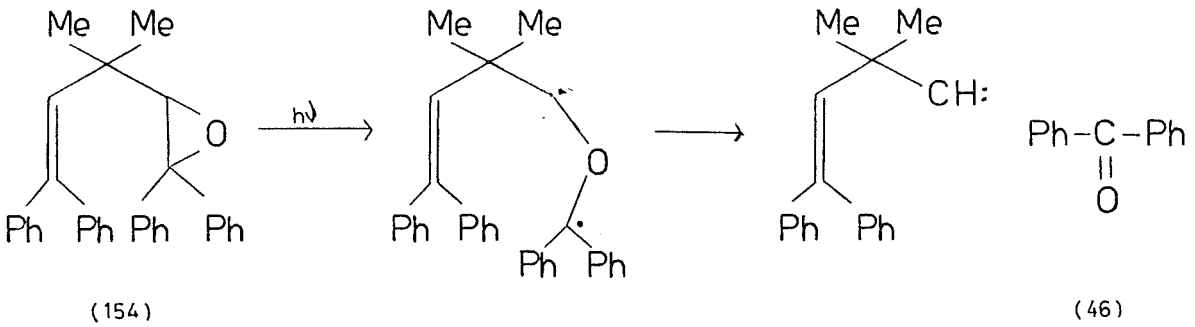
The epoxide(154) is an unstable molecule and decomposes at room temperature within 24hr. It decomposes at 4°C in two weeks.

The di-epoxide(155) was identified from its ^{1}Hn.m.r. spectrum which showed peaks for two methyl groups(δ_H0.59, 0.78), for the epoxide proton(δ_H2.95) and for the aromatic protons (δ_H7.18). This epoxide decomposed at 4°C over a period of two days and was not studied further.

The mono-epoxide(154) was irradiated in deoxygenated benzene under a nitrogen atmosphere and the reaction was monitored by g.l.c. and t.l.c. After 3.5hr, no epoxide remained. The photolysis residue was absorbed onto an alumina column but elution gave no products in sufficiently large quantities to be identified. Irradiation of the epoxide(154) in light petroleum for 2hr gave no reaction but after irradiation for a further 7hr no epoxide remained. The ^{1}Hn.m.r. spectrum of the crude reaction mixture showed the presence of an aldehyde proton(δ_H9.33, J 2.5Hz) which was coupled to a single proton(δ_H4.75, J 2.5Hz). The i.r. spectrum of the reaction mixture also showed the presence of

the aldehyde(ν 2720, 1725 cm^{-1}). The only product isolated and identified after chromotography of the reaction mixture was benzophenone(46) which could be identified by comparison of its spectra with those obtained for an authentic sample.

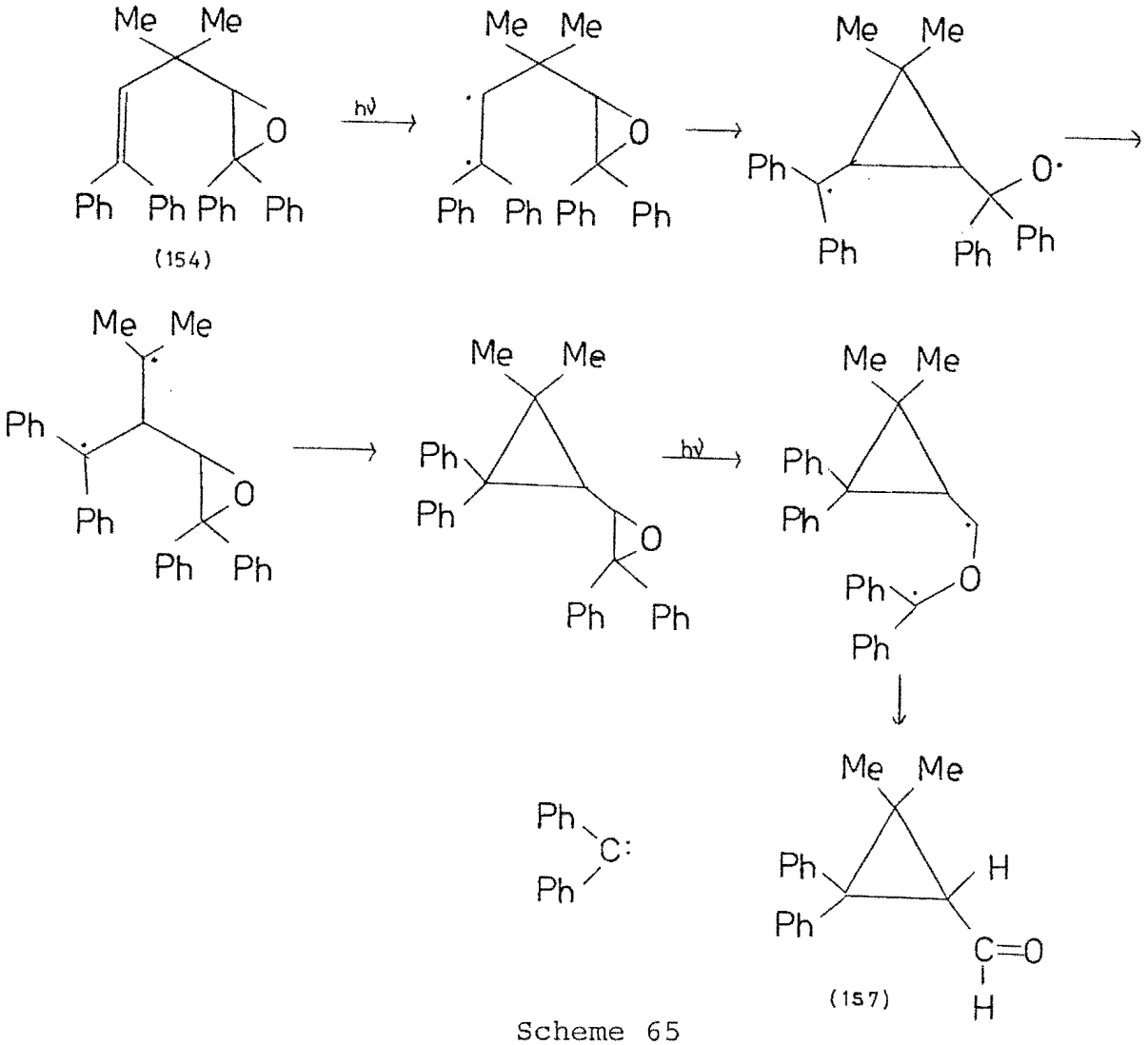
Benzophenone(46) can be formed by the photoinduced cleavage of the C-C bond of the epoxide ring and subsequent



Scheme 64

C4-O cleavage(Scheme 64). Fragmentation of phenyl substituted epoxides on irradiation has been observed for other systems[20].

The formation of an aldehyde in which the aldehydic proton is coupled to a neighbouring proton requires rearrangement of the skeleton of the molecule. The structure of the product must remain in doubt since it was not possible to isolate it. One possible mechanism by which such an aldehyde could be formed is depicted in Scheme 65. The mechanism is analogous to the di-π-methane rearrangement observed for 1,4-dienes and involves initial excitation of the vinyl bond and bridging to form a cyclopropyl dicarbinyl diradical(156). Opening of the ring enables the epoxide ring to recyclise and the product expected for a di-π-methane type rearrangement results. Subsequent photolysis of the aryl substituted epoxide ring leads to the formation of the aldehyde(157) and a carbene.



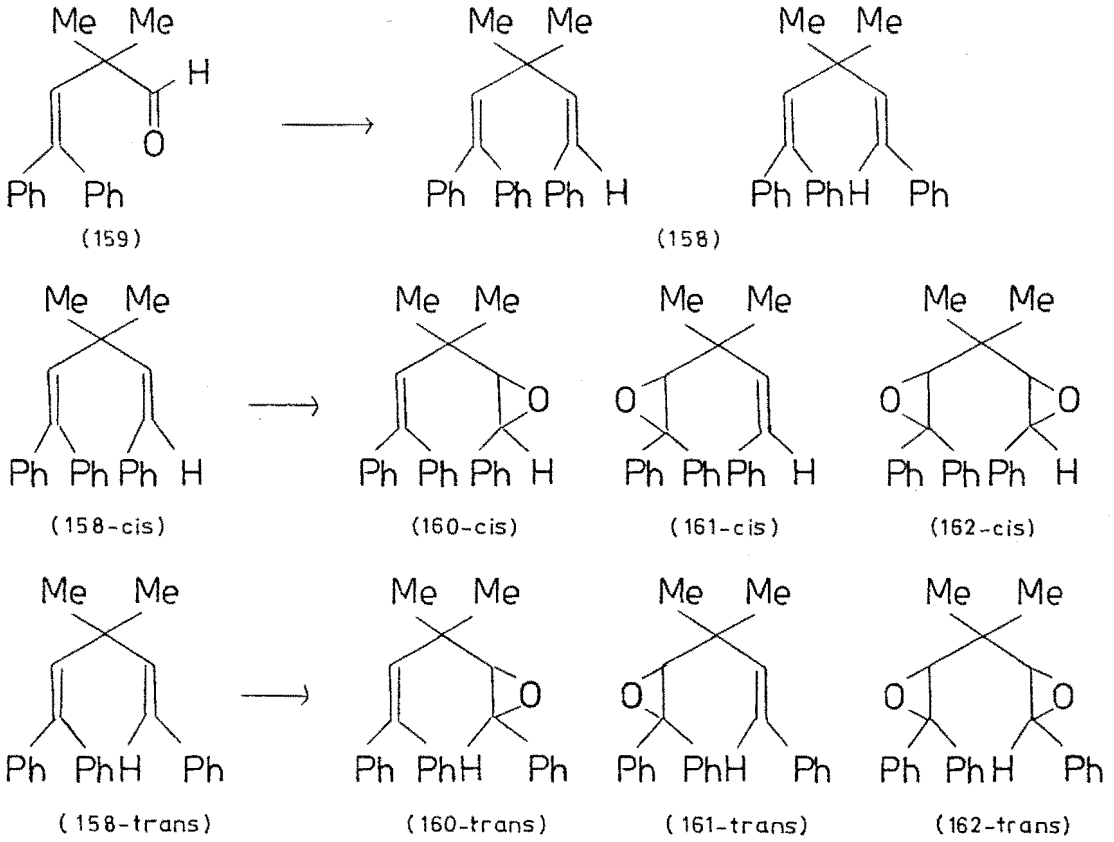
Scheme 65

(b) 3,3-DiMethyl-4,5-epoxy-1,1,5-triphenylpent-1-ene(161) and 3,3-dimethyl-4,5-epoxy-1,5,5-triphenylpent-1-ene(160)

The *cis*- and *trans*- isomers of 3,3-dimethyl-1,1,5-triphenylpenta-1,4-diene(158) were prepared by a Wittig reaction of benzyltriphenylphosphonium chloride on 2,2-dimethyl-4,4-diphenylbut-3-enal(159)[4]. The separation of the two isomers by chromotography on silver nitrate alumina was unsuccessful and only a small amount of *cis*-alkene was obtained sufficiently

pure for full spectral analysis. The ^{1}Hn.m.r. spectrum of *cis*-3,3-dimethyl-1,1,5-triphenylpenta-1,4-diene(158-*cis*) showed one signal due to the methyl protons(δ_H1.05), an AB quartet (δ_H5.45, 6.19, J 12Hz) and a singlet(δ_H6.02) due to the vinyl protons and a multiplet centered at δ_H7.20(Wh/2 4Hz) for the aromatic protons. The ^{1}Hn.m.r. spectrum of the *trans*-isomer (158-*trans*) showed resonances for the methyl protons(δ_H1.15), a singlet for H4 and H5 at δ_H6.09, H2 at δ_H6.11 and for the aromatic protons at δ_H7.20.

Reaction of a mixture of the diene isomers with monoperphthalic acid resulted in epoxidation of both alkene bonds. Four mono-epoxide isomers and three diepoxide isomers were detected and identified from the reaction mixture(Scheme 66).

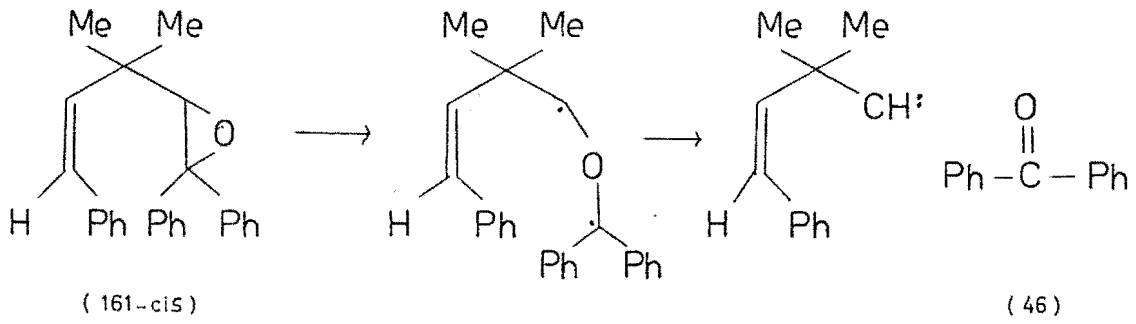


Scheme 66

The epoxides(160, 161, 162) were separated by column chromotography although some isomers could not be separated sufficiently pure for full spectral analysis. The *cis*-epoxide (161) was isolated in sufficient quantity for photochemical reaction. The *trans*-epoxide(161) could not be separated from the *cis*-isomer(161) and its photochemistry was not examined. Only small quantities of the *cis*- and *trans*-epoxides(160) were isolated from each other enabling identification by spectral analysis. A mixture of the isomers of (160) was examined photochemically. The di-epoxides(162) could be separated from the mono-epoxides(161, 160) but were found to be unstable at room temperature over 12hr.

The ^{1}Hn.m.r. spectrum of *cis*-3,3-dimethyl-4,5-epoxy-1, 5,5-triphenylpent-1-ene(161-*cis*) showed the presence of two methyl signals(δ_H0.79, 0.92) and a single epoxide proton peak (δ_H3.19). The two vinyl protons appeared as an AB quartet (δ_H5.34, 6.24, J 13Hz) and the aromatic protons as two singlet peaks(δ_H7.08, ClArH's; δ_H7.22, C5ArH's). The infrared spectrum showed the presence of the epoxide moiety(ν 1250 cm^{-1}) and the vinyl bond(ν 710 cm^{-1}). The ^{13}Cn.m.r. spectrum showed the presence of two methyl carbon resonances(δ_C26.5, 26.8) and three phenyl rings by twelve peaks. The C3 signal appeared at δ_C38.4, the epoxide carbon peaks at δ_C74.6(C4) and δ_C66.5(C5) and the vinyl carbon resonances at δ_C128.4(C1) and δ_C137.0(C2).

Photolysis of this epoxide(161-*cis*) was carried out in light petroleum for 11hr while the reaction was monitored by g.l.c. The only product isolated on column chromotography was benzophenone(46)(6.4%) which would be formed by cleavage of the C-C bond of the epoxide ring followed by C-O bond cleavage (Scheme 67) as expected for the photolysis of an aryl substituted epoxide[20].



(161-cis) (46)

Scheme 67

As previously noted, the *trans*-isomer(161) could not be isolated from the *cis*-epoxide(161) and hence a photochemical reaction of it was not attempted. The ^{1}Hn.m.r. spectrum of the impure *trans*-3,3-dimethyl-4,5-epoxy-1,5,5-triphenylpent-1-ene(161-*trans*) showed the presence of the methyl proton signals (δ_H0.97, 1.11) while the aromatic protons appeared as two singlet peaks(δ_H7.15, C5ArH's; δ_H7.27, ClArH's). The epoxide proton peak appeared at δ_H3.22 and the vinyl protons absorbed at δ_H6.00 and δ_H6.05.

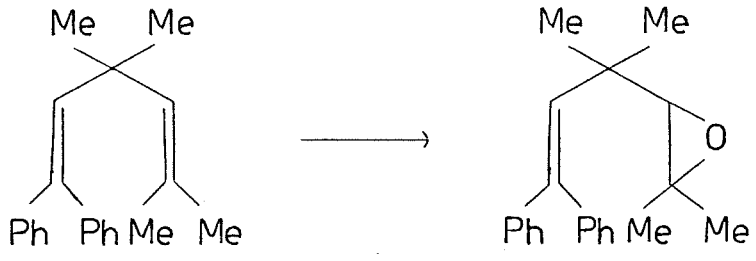
As noted previously, only small quantities of each of the isomers of the aryl epoxide(160) were isolated in pure form. The ^{1}Hn.m.r. spectrum of *trans*-3,3-dimethyl-4,5-epoxy-1,1,5-triphenylpent-1-ene(160-*trans*) showed two methyl signals (δ_H0.95, 1.00). The epoxide protons appeared as a AB quartet (δ_H 2.80, 3.63, J 2Hz) and the vinyl proton signal appeared at δ_H 6.03. The aromatic protons appeared as a multiplet(Wh/2 12Hz) centered at δ_H7.10. The ^{1}Hn.m.r. spectrum of *cis*-3,3-dimethyl-4,5-epoxy-1,1,5-triphenylpent-1-ene(160-*cis*) showed a single methyl signal(δ_H0.75), the vinyl proton peak(δ_H5.75) and a multiplet due to the aromatic protons(δ_H7.15, Wh/2 12Hz). The epoxide protons appeared as an AB quartet(δ_H2.95, 3.95, J 4Hz).

Photolysis of a mixture of the *cis* and *trans* isomers (160)(c.2:1) in benzene for 5hr showed little reaction. The ^{1}Hn.m.r. spectrum of the reaction mixture showed that the ratio of isomers changed to c.3:1 as determined by integration of the epoxide and vinyl protons resonances. The only product isolated by column chromotography was the *cis* epoxide(160-*cis*).

Two isomers of *trans*-1,2-4,5-diepoxy-3,3-dimethyl-1,1,5-triphenylpentane(162-*trans*) and one *cis* isomer(162-*cis*) were isolated but proved to be unstable at 4^{o}C and decomposed over the period of two days. Difficulties such as these in handling and separation of the mono-epoxides limited the study of them.

(c) 1,1-Diphenyl-4,5-epoxy-3,3,5-trimethylhex-1-ene(163)

1,1-Diphenyl-3,3,5-trimethylhexa-1,4-diene(5) was prepared by standard methods[4] and reacted with monoperphthalic acid to give 1,1-diphenyl-4,5-epoxy-3,3,5-trimethylhex-1-ene(163) as the only product. The ^{1}Hn.m.r. spectrum of the epoxide(163)



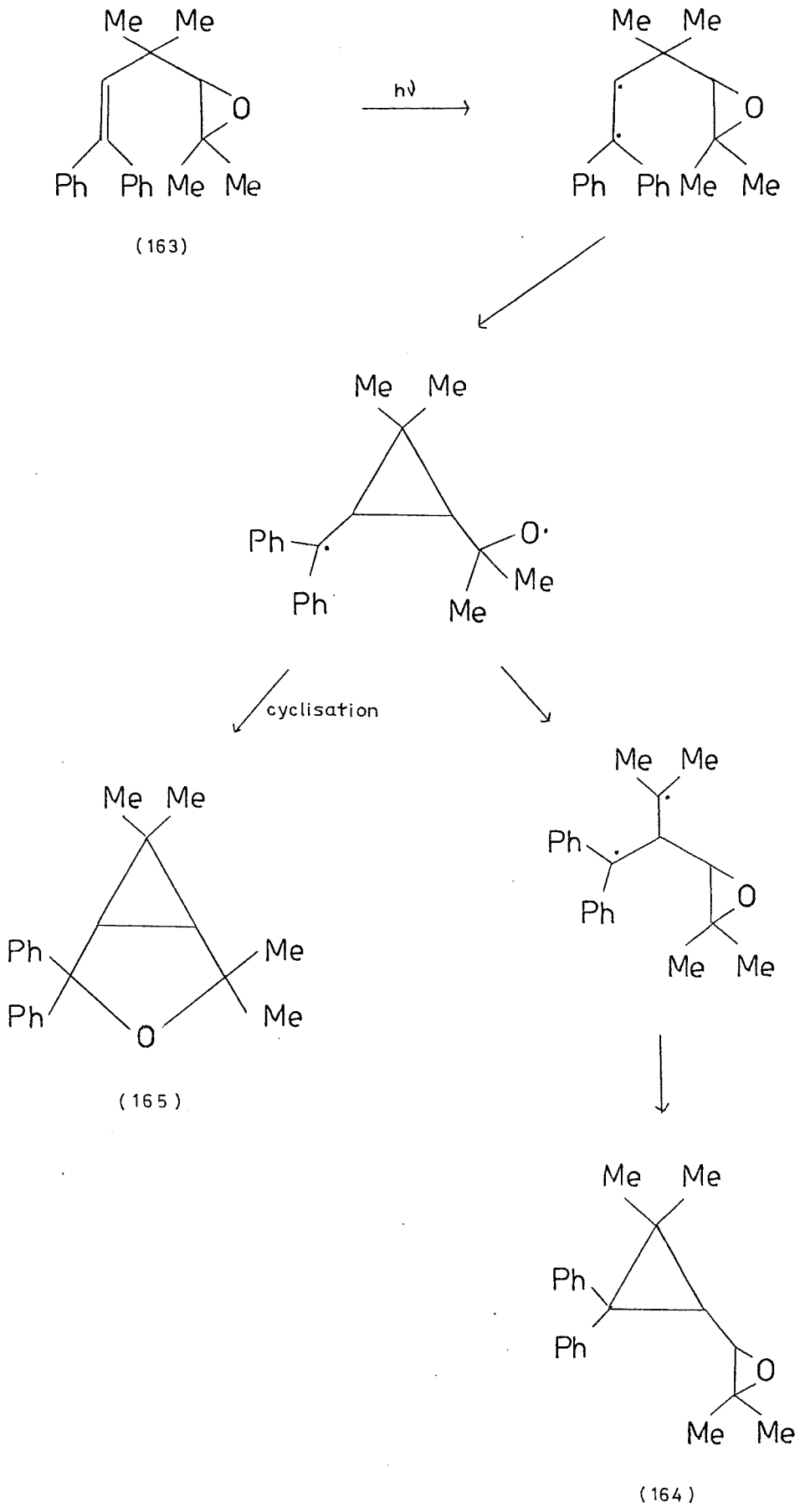
(5) (163)

showed a singlet peak due to the C3 methyl protons(δ_H1.12) and peaks due to the epoxide methyl protons(δ_H0.92, 1.37). The epoxide proton signal appeared at δ_H2.52, the vinyl proton absorption at δ_H6.12 and signal due to the aromatic protons

at δ_H7.07. The ^{13}Cn.m.r. spectrum showed the C3 methyl (δ_C26.6, 28.9) and the C5 methyl(δ_C18.8, 26.4) signals. The vinyl carbon resonances appeared at δ_C139.1(C1) and δ_C134.9(C2), the epoxide carbon peaks at δ_C72.8(C4) and δ_C59.1(C5) and C3 at δ_C37.2. The aromatic carbon signals appeared as eight peaks.

Photolysis of the epoxide(163) in light petroleum for 10hr gave no reaction as shown by ^{1}Hn.m.r. spectroscopy of the reaction mixture. The epoxide(163) was then photolysed for 5hr in acetone. Chromotography enabled unreacted epoxide(163)(53%) to be separated from a product(30%) which was shown from the ^{1}Hn.m.r. spectrum to contain eight methyl groups(δ_H0.68, 0.70, 0.80, 1.03, 1.15, 1.17, 1.30, 1.43), four methine protons(δ_H2.33, 2.51, 3.13, 3.22) and four phenyl rings (δ_H7.23, Wh/2 5Hz). The ^{13}Cn.m.r. spectrum similarly showed resonances for eight methyl groups(δ_C19.3, 19.6, 21.3, 21.9, 22.6, 23.7, 26.7), six quaternary carbons(δ_C35.8, 36.3,59.2, 59.7, 66.6, 69.7), four methine carbons(δ_C69.7, 70.4, 71.2, 72.8) and aromatic carbons. The multiplicity of the ^{1}Hn.m.r. and ^{13}Cn.m.r. spectra suggested that the product was a mixture of two components. However, t.l.c. failed to separate this mixture. The absence of a vinyl proton signal in the ^{1}Hn.m.r. spectrum suggested that a skeletal rearrangement had occurred and the upfield position of peaks for the product protons (δ_H2.23, 2.51) suggested that a cyclopropane ring may have been formed.

The product remains unidentified, although structures(164) and (165) which could be formed as shown in Scheme 68, are possibilities.



(163)

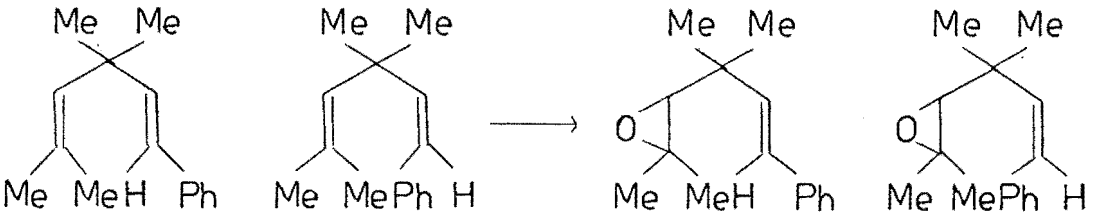
(165)

(164)

Scheme 68

(d) 4,5-Epoxy-1-phenyl-3,3,5-trimethylhex-1-ene(166)

A mixture of *cis*- and *trans*-1-phenyl-3,3,5-trimethylhexa-1,4-diene(13) was prepared[7] and reacted with monoperphthalic acid to give *cis*- and *trans*-4,5-epoxy-1-phenyl-3,3,5-trimethylhex-1-ene(166). Only small quantities of each of the isomers could be isolated in pure form. The ^{1}Hn.m.r. spectrum of the *cis*-epoxide(166-*cis*) showed the presence of



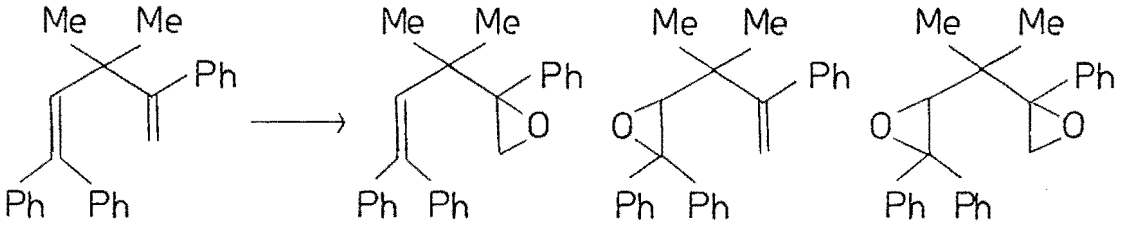
(13) (166)

resonances for four methyl groups(δ_H1.03, 1.06, 1.10, 1.33), for the epoxide proton(δ_H2.54) and for the aromatic protons (δ_H7.20). The vinyl protons appeared as an AB quartet(δ_H5.60, 6.42, J 12.5Hz). The ^{1}Hn.m.r. spectrum of the *trans*-epoxide (166-*trans*) showed three methyl signals(δ_H1.13, 1.33, 1.36), together with signals for the epoxide proton(δ_H2.62), the vinyl protons(δ_H6.28) and for the aromatic protons(δ_H7.30).

Photolysis of a mixture of *cis* and *trans* epoxides(166) (c.4:11) in benzene for 4 hr showed only *cis-trans* isomerisation of the alkene moiety. The ^{1}Hn.m.r. spectrum of the reaction product showed the *cis* and *trans* isomers in the ratio c.1:1 by integration of the epoxide and vinyl proton signals. Photolysis of a mixture of *cis* and *trans* epoxides(166)(c.1:1) in acetone for 5.5hr also showed only *cis* - *trans* isomerisation of the alkene moiety. The ^{1}Hn.m.r. spectrum of the reaction product showed the *cis* and *trans* isomers in the ratio c.2:1.

(e) 3,3-Dimethyl-4,5-epoxy-2,5,5-triphenylpent-1-ene(169) and 3,3-dimethyl-4,5-epoxy-1,1,4-triphenylpent-1-ene(168)

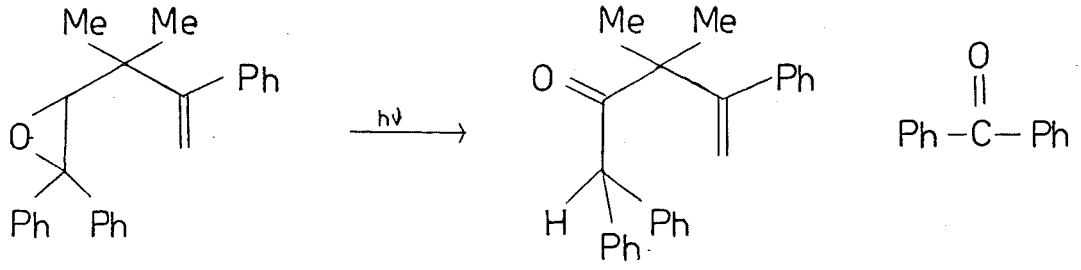
3,3-Dimethyl-1,1,4-triphenylpenta-1,4-diene(167) was prepared[87] and reacted with *m*-chloroperbenzoic acid to give epoxidation on both vinyl bonds. The isomers were separated by column chromotography.



(167) (168) (169) (170)

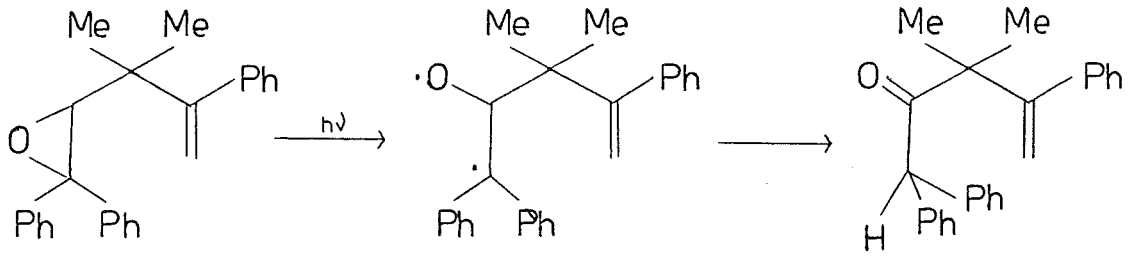
The ^{1}Hn.m.r. spectrum of 3,3-dimethyl-4,5-epoxy-2,5,5-triphenylpent-1-ene(169) showed the presence of the methyl signals(δ_H0.65, 1.00) and a multiplet for the aromatic protons (δ_H7.31, Wh/2 8Hz). The epoxide proton peak appeared at δ_H3.37 and the vinyl protons showed resonances at δ_H4.96 and δ_H5.39 (J 1.5Hz). The ^{13}Cn.m.r. spectrum showed the presence of the methyl carbon signals(δ_C26.8, 22.1) and the aromatic carbons appeared as nine peaks. The epoxide carbon signals appeared at δ_C73.6(C4) and δ_C66.5(C5), and the peaks for the vinyl carbons at δ_C113.8(C1) and δ_C156.6(C2) and for C3 at δ_C41.3.

The diphenyl substituted epoxide(169) was unreactive on photolysis in benzene solution for 8hr. Irradiation of the epoxide(169) in acetone solution for 6hr gave unreacted epoxide(169)(19%), benzophenone(46)(19%) and 3,3-dimethyl-2,5,5-triphenylpent-1-en-4-one(171)(19%). The ^{1}Hn.m.r. spectrum of the ketone(171) showed a single peak for the methyl protons (δ_H1.22) and the aromatic protons appeared as a multiplet



(169) (171) (46)

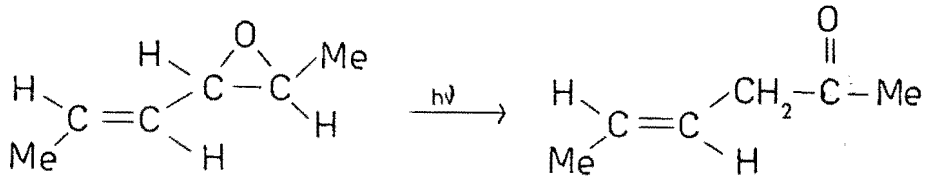
centered at δ_H7.13(Wh/2 10Hz). The signals for the vinyl protons appeared at δ_H5.29 and δ_H5.31 and for H5 at δ_H5.57. The i.r. spectrum showed the presence of the carbonyl group (ν 1710 cm^{-1}) and the terminal vinyl group(ν 1660, 900 cm^{-1}). The ^{13}Cn.m.r. spectrum showed the methyl carbon signals(δ_C25.3) and the aromatic carbons as five peaks. The signal for the terminal vinyl carbon appeared at δ_C117.2, for the carbonyl carbon at δ_C210.3, for C3 at δ_C54.8 and C5 at δ_C57.8. The ketone(171) is formed by C5-O bond cleavage followed by hydrogen migration(Scheme 69).



(169) (171)

Scheme 69

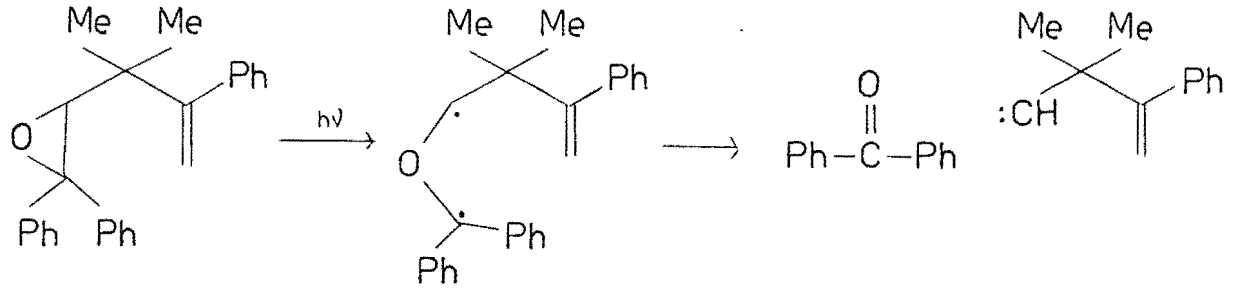
Radical 1,2-hydrogen migration shifts are symmetry forbidden in ground state diradicals[32] but have been observed for the photorearrangement of styrene oxide(41) to acetophenone(42)[18] and α,β-unsaturated epoxides(61) to α,β-unsaturated ketones(62)[30].



(61) (62)

It was proposed[30] that a 1,2-radical migration might be favourable starting from a 1,3-diradical since the energy gained from concurrent formation of the carbonyl group may overcome the orbital symmetry considerations.

Benzophenone(46) is formed from epoxide(169) by C-C bond cleavage of the epoxide ring followed by C-O bond cleavage resulting in the formation of the ketone and carbene(Scheme 70).



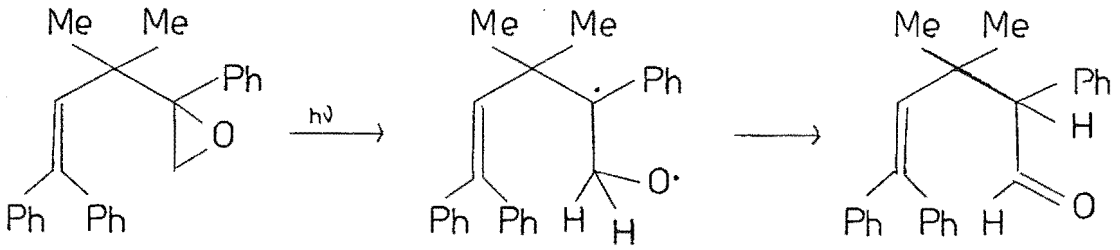
(169) (46)

Scheme 70

The other isomer(168) formed on epoxidation of the diene(167) was similarly photolysed. The ^{1}Hn.m.r. spectrum of 3,3-dimethyl-4,5-epoxy-1,1,4-triphenylpent-1-ene(168) showed the methyl groups as a single peak(δ_H0.89) and the aromatic protons as a narrow multiplet(δ_H7.10, Wh/2 3Hz). The epoxide proton signals appeared at δ_H2.61 and δ_H3.03(J 5Hz) and the vinyl proton peak at δ_H6.10. The ^{13}Cn.m.r. spectrum

showed the resonances for two methyl carbons(δ_C25.0, 25.4) and the aromatic carbons appeared as eleven peaks. The signals for the epoxide carbons appeared at δ_C66.4(C4) and δ_C51.2(C5), for the vinyl carbons at δ_C139.4(C1) and δ_C134.6(C2) and for C3 at δ_C40.8.

Photolysis of the epoxide(168) in benzene solution showed no reaction after 11hr. An acetone solution of the epoxide(168) was irradiated for 8hr. The ^{1}Hn.m.r. and i.r. spectra of the reaction mixture showed that rearrangement of the epoxide(168) had occurred. An aldehyde proton signal δ_H9.97 (Wh/2 4Hz) coupled to a peak at δ_H3.47 (Wh/2 4Hz) was detected in the ^{1}Hn.m.r. spectrum. The i.r. spectrum(ν 1720, 2720 cm^{-1}) similarly showed the presence of an aldehyde. Nothing could be isolated in sufficient quantity for identification by column chromotography. The aldehyde(c.50%) detected in the crude mixture is assumed to be 3,3-dimethyl-2,5,5-triphenylbut-4-enal(172) which could be formed by C2-O bond cleavage and hydrogen migration(Scheme 71).



(168) (172)

Scheme 71

Conclusion

The photolyses of this series of epoxides(154,160,161, 163,166,168,169) show reaction pathways typical of the epoxide moiety. The more reactive diphenyl substituted epoxides undergo both C-C and C-O bond cleavage of the epoxide ring. C-C Bond cleavage is illustrated by the formation of benzophenone and is expected to be accompanied by the formation of carbenes[20]. C-O Bond cleavage followed by group migration results in the formation of aldehyde and ketone products which have been observed in and sometimes isolated from the reaction mixtures. These products are themselves photolabile and undergo further fragmentation. The very low yields of product isolated is the result of this fragmentation and polymerisation and the unstable nature of the products formed. Some of the products observed in the reaction mixtures of these β,γ-unsaturated epoxides indicate possible interaction between the vinyl and epoxide moieties as described in Schemes 56 and 68.

PART II

Acid Catalysed Rearrangements of Epoxides

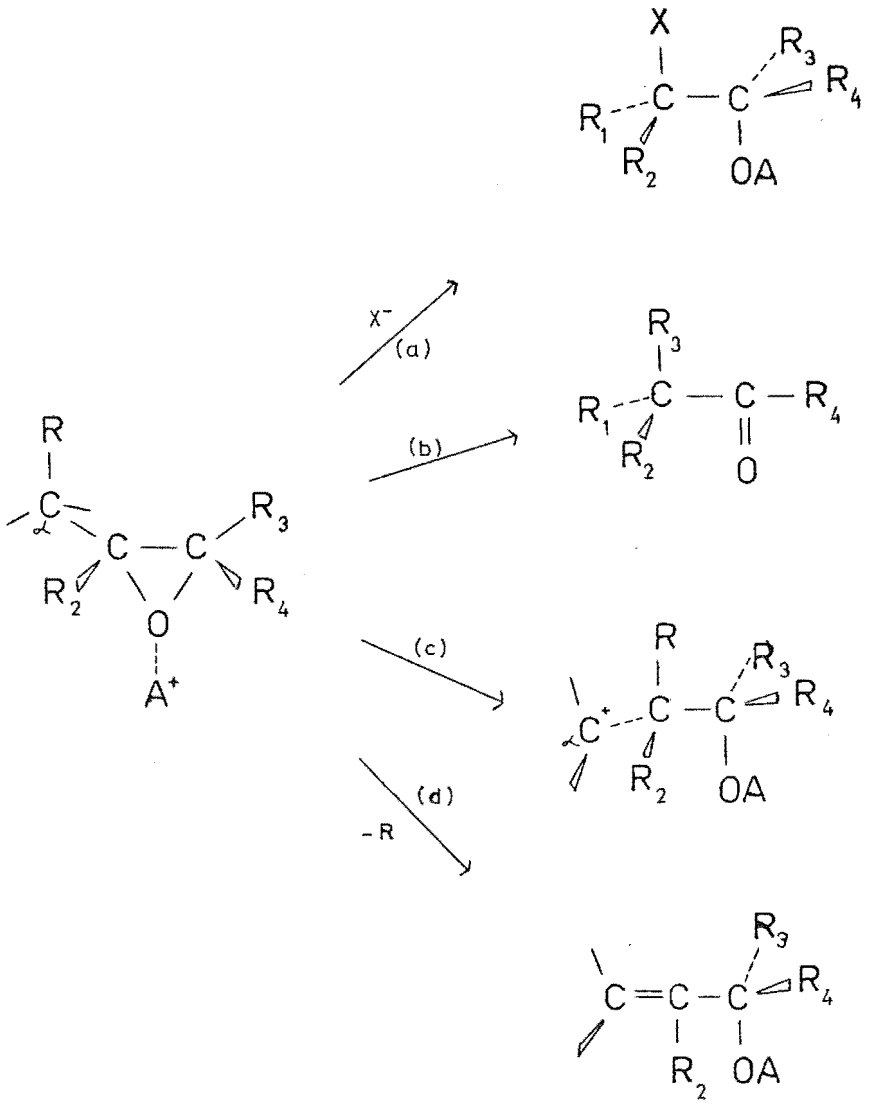
In the course of the studies on the photochemistry of the bifunctional alkene-epoxide systems, several *trans*-1-aryl-1, 2-epoxy-3-methyl-3-phenylbutanes(89) were prepared. In order to prepare an authentic sample of 1,3-diphenyl-3-methylbutan-2-one(146a) the epoxide(89a) was reacted with BF_3-etherate. The unusual results obtained for this reaction prompted a further examination of the acid catalysed chemistry of these systems.

The chemistry of epoxides has been extensively studied and with acids the following reactions are well documented: (a) attack by an external nucleophile, X^-; (b) migration of a substituent from one carbon of the epoxide ring to the other to give a carbonyl compound; (c) the 1,2-shift of a group from the α-carbon atom of one of the substituents to the carbon atom involved in C-O cleavage; (d) elimination of a group from the α-carbon of one of the substituents with the formation of a double bond.

The orientation of ring opening is determined principally by the relative combined electron releasing power of the substituents on each epoxide-carbon[88], opening being favoured at tertiary > secondary > primary centers. Kayser and Morand[89] discuss the nucleophilic attack on an epoxide in terms of the hard-soft acid-base principle. Coordination of the 'hard' acid to the oxygen of unsymmetrically substituted epoxides leads to a positive charge developing at the carbon atom best suited to accommodate it. 'Soft' nucleophiles attack selectively at the 'softer' carbon which has developed some positive charge. 'Hard' nucleophiles are less selective and show preference for the sterically more accessible carbon.

The choice of the migrating substituent R_3 or R_4(path (b), Scheme 72) is determined by their relative migratory aptitudes

and steric environment. Migratory aptitudes follow the general trend, aryl > acyl > hydrogen > alkyl, observed in all reactions involving 1,2-shifts to electron deficient centers[88].

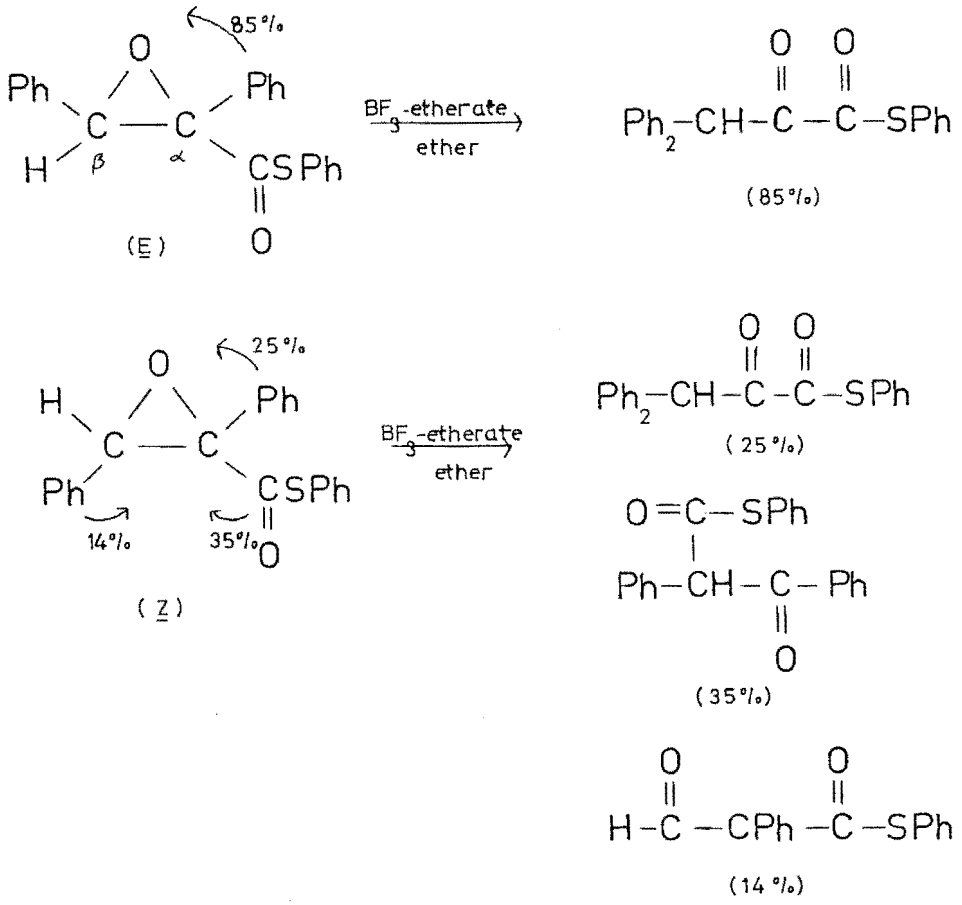


Scheme 72

The strong substituent effect controlling the orientation of opening suggests that a large degree of charge separation takes place in the transition state. There is strong evidence that the reaction of acid or Lewis acids with epoxides occurs *via* an intermediate carbocation[90]. Several acyclic epoxides rearrange to give products where the configuration at the epoxide carbon is retained[91] and several steroidal exocyclic methylene epoxides have been shown to give products of both inversion and retention of

configuration at the tertiary carbon[92].

There is also some evidence that the epoxide reaction may be concerted. The BF_3 induced rearrangement of optically active ethyl 2-methyl-3-phenylglycidate occurs by migration of the carbethoxy group with retention of optical purity[93]. Gorski, Dagli and Wemple[94] found a preference for Cβ-O cleavage in the treatment of the *E* and *Z* isomers of S-phenyl-2, 3-diphenylthiolglycidate with BF_3-etherate but the product mixture was dependent on the stereochemistry at C_α suggesting that steric interactions are important(Scheme 73).



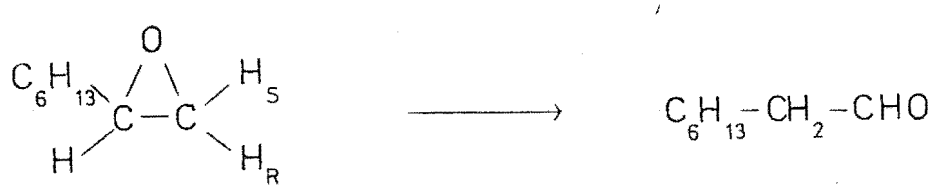
Scheme 73

The stereochemical specificity in the acid catalysed rearrangement of *cis*- and *trans*-2,3-epoxybutanes, whereby there is a greater tendency for the methyl to migrate in the *trans* epoxide than the *cis* epoxide[95-97] has been cited[98] as evidence for the reaction occurring *via* some type of bridged

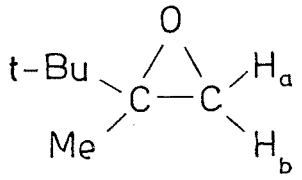
intermediate (the 'concerted' pathway) rather than *via* an open carbocation. However, short-lived carbocations have been noted to rearrange stereoselectively in cases where marked conformational preference exist in the substrate[99,100]. If the opening of the epoxybutanes did give carbocation intermediates, these would have different initial conformations and their rapid rearrangement might be expected to occur with some sort of stereoselectivity.

Blackett[101] found that the BF_3 catalysed rearrangement of 1,2-epoxy-2,3,3-trimethylbutane(174) to give 2,3,3-trimethylbutanal(175) proceeded by selective (c.1.9:1) migration of the hydrogen atom(H_b) *cis* to the methyl group by studying the rearrangements of the monodeuterated epoxides(176, 177). He determined that the relative rates of hydride migration and of conformational change for the rearrangement of the epoxide were of significance in the rearrangements of carbocations generated in acyclic systems(Scheme 74).

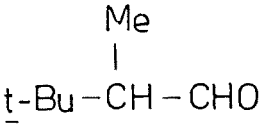
Lim[102] found that the BF_3-etherate catalysed rearrangement of 1,2-epoxyoctane(178) to give octanal(179) proceeds by selective(c.1.4:1) migration of the prochiral hydrogen *trans* to the alkyl group. Stereoselectivity is expected if the rate of hydride migration were comparable with the rate of rotation about the C1-C2 bond since with the favoured rotation mode, analogous to Scheme 74, the pro-R-chiral hydrogen(H_R) has the opportunity to migrate before H_S.



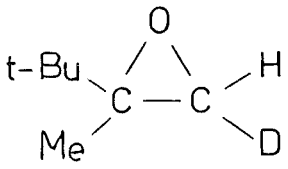
(178) (179)

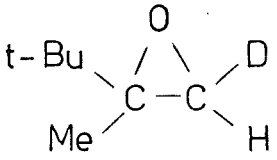


$\xrightarrow{BF_3\text{-etherate}}$

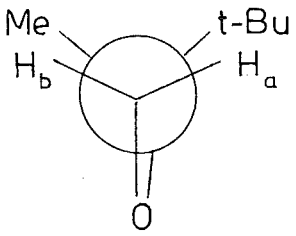


(174) (175)

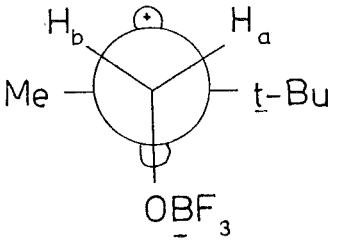




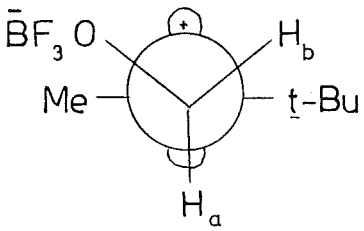
(176) (177)



$\xrightarrow[BF_3\text{-etherate}]{\text{slow}}$



$\rightleftharpoons$



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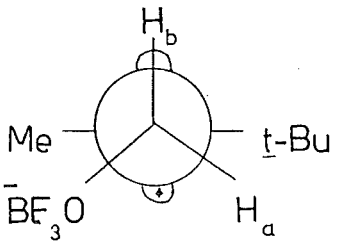


$\downarrow k_{H_a}$ $\downarrow k_{H_b}$

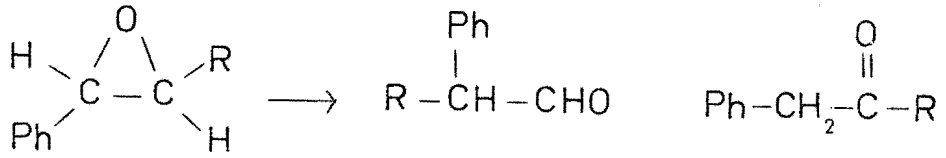
aldehyde aldehyde

(175) (175)

Scheme 74

If rotation about the C1-C2 bond was rapid relative to hydride migration no stereoselection of the prochiral hydrogen would be observed.

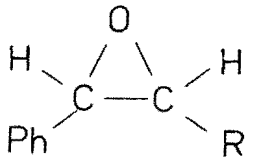
In a study of the BF_3-etherate catalysed rearrangement of *trans*-β-alkyl-styrene epoxides(180) to aldehyde(181) and ketone(182) products, Kelly[103] found that for a small alkyl group(R = Me, Et), a change in the reaction medium from ether to benzene had no significant effect on the product distribution whereas the larger alkyl groups(R = *iso*-Pr, *t*-Bu) displayed a significant increase in alkyl migration. He suggested that



(180) (181) (182)

R = Me, Et, iso-Pr, t-Bu

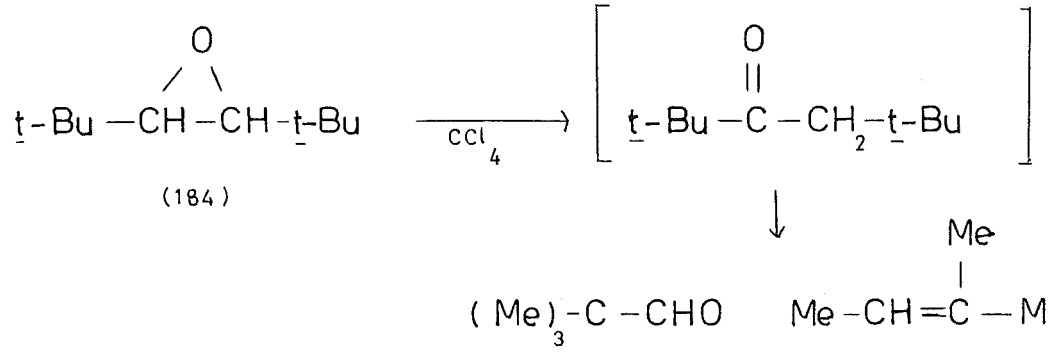
carbocation development was more marked for the larger alkyl groups which are expected to migrate more easily than the smaller groups because of their increased ability to stablise the transition state. However, for the same series of *cis*-β-alkyl-styrene epoxides(183), a change in the reaction medium from ether to benzene had no effect on the product distribution.



(183)

R = Me, Et, iso-Pr, t-Bu

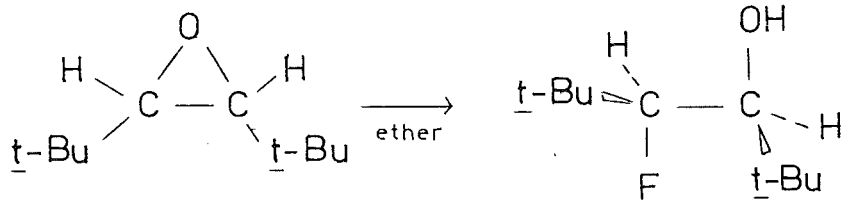
Swallow *et al*[97] also found that solvent was important in determining the reaction pathway. Reaction of *trans*- and *cis*-1,2- *t* -butylethylene oxide(184) with BF_3-etherate in carbon tetrachloride gave pivalaldehyde(185) and 2-methylbut-2-ene(186) while in ether the *cis* epoxide(184-*cis*) rearranged to give a fluorohydrin(187) and the *trans* epoxide(184-*trans*) did not react.



(184)

(185)

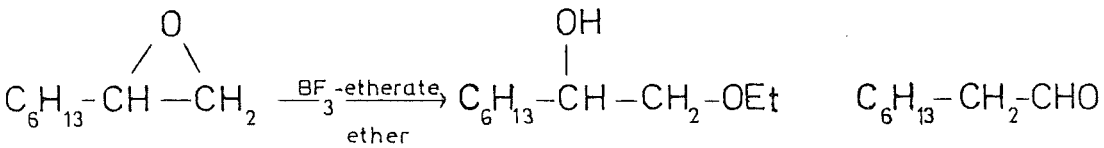
(186)



(184-cis)

(187)

Lim[102] found that the BF_3-etherate catalysed rearrangement of 1,2-epoxyoctane(178) in ether gave 1-ethanoxy-octan-2-ol(188)(60%) and octanal(179)(12%) whereas for the reaction of the epoxide(178) in dioxane only aldehyde(179) was isolated.



(178)

(188)(60%)

(179)(12%)

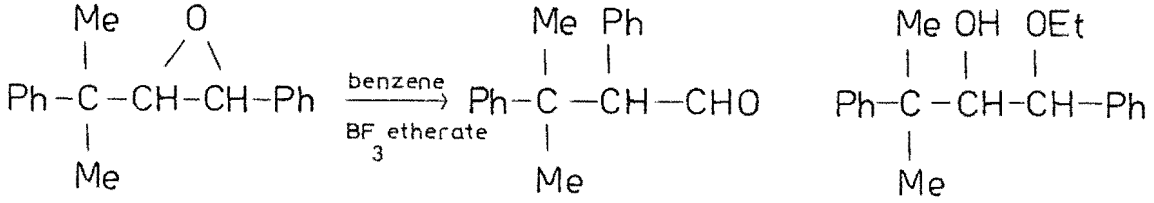
DISCUSSION

BF_3-etherate Catalysed Rearrangement of 1-Aryl-1,2-epoxy-3-methyl-3-phenylbutanes

In this discussion the reaction of *trans*-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a) with BF_3-etherate in benzene is covered first(p. 117) and is followed by the examination of this epoxide's(89a) reaction with BF_3-etherate in ether(p.133). The reactions of the Cl-aryl substituted *trans* epoxides(89) are similarly described, firstly for rearrangement in benzene (p.144) and then in ether(p.148). Reactions of the *cis* epoxides(216) with BF_3-etherate in benzene are described from p.151.

(a) Reaction of *trans*-1,3-diphenyl-1,2-epoxy-3-methyl-3-phenylbutane(89a) with BF_3-etherate in benzene.

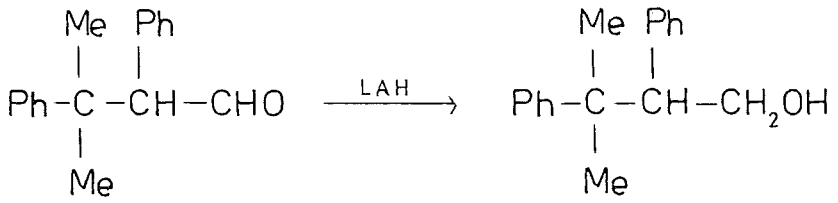
From the reaction of *trans*-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a) with BF_3-etherate in benzene, 2,3-diphenyl-3-methylbutanal(140a)(43%) and ($1R^*$, $2R^*$)-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(189a)(13%) were isolated.



(89a) (140a)(43%) (189a)(13%)

The aldehyde(140a) which was somewhat unstable and

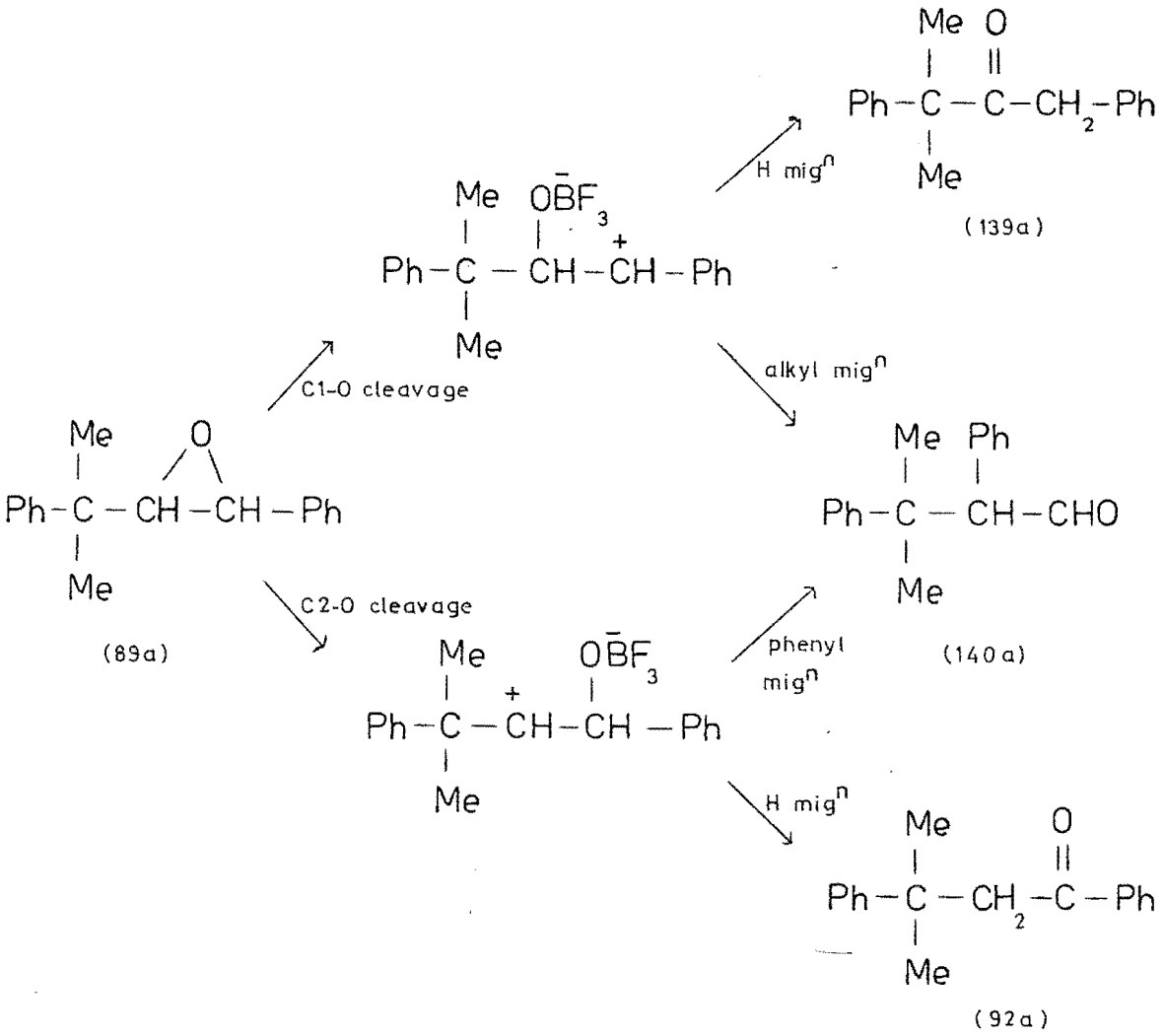
decomposed with time, was identified by its i.r. spectrum which showed a carbonyl stretch at ν 1715 cm^{-1} and the aldehyde proton stretch at ν 2720 cm^{-1}. The ^{1}Hn.m.r. spectrum showed the aldehyde proton signal(δ_H9.79, J 3Hz) coupled to the H2 signal (δ_H3.72, J 3Hz). The methyl groups appeared as singlet peaks (δ_H1.40, 1.45) and the aromatic protons as a narrow multiplet (δ_H7.08, Wh/2 3Hz). The ^{13}Cn.m.r. spectrum exhibited resonances for a carbonyl carbon(δ_C201.7), for a methine carbon (δ_C68.6), a quaternary carbon(δ_C41.2), two methyl carbons(δ_C25.7, δ_C27.7) and for the aromatic rings(C2Ar:δ_C134.5, 130.6, 127.9, 127.3; C3Ar: δ_C146.1, 126.6, 128.1, 126.4). Reduction of the aldehyde(140a) with lithium aluminium hydride gave 2,3-diphenyl-3-methylbutan-1-ol(153a). The i.r. spectrum of the alcohol (153a) showed the presence of hydroxyl(ν 3620 cm^{-1}). The



(140a) (153a)

^{1}Hn.m.r. spectrum showed H2 as a doublet of doublets(δ_H3.08, J 10Hz, J 5Hz) and the C1 protons appeared as a complex multiplet centered at δ_H3.77(Wh/2 15Hz). The methyls appeared as singlet peaks(δ_H1.20, 1.28) and the two aromatic rings as a narrow multiplet(δ_H7.19, Wh/2 3Hz). The ^{13}Cn.m.r. spectrum supported the structure of the alcohol(153a) with the signals for C1 at δ_C62.5 and for C2 at δ_C59.4. Two methyl carbon resonances appeared at δ_C28.9 and δ_C24.0, the quaternary C3 signal at δ_C40.1 and the two aromatic rings appeared as eight peaks(C2Ar: δ_C139.2, 130.1, 127.9, 126.7; C3Ar:δ_C148.0, 126.3, 128.0, 125.8).

BF_3-etherate catalysed ring opening of the epoxide(89a) was expected to involve either C1-O bond cleavage followed by hydrogen migration to give 1,3-diphenyl-3-methylbutan-2-one(139a) and alkyl migration to give 2,3-diphenyl-3-methylbutanal(140a) or C2-O bond cleavage followed by hydrogen migration to give 1,3-diphenyl-3-methylbutan-1-one(92a) and aryl migration to give the aldehyde(140a)(Scheme 75). The ketone products

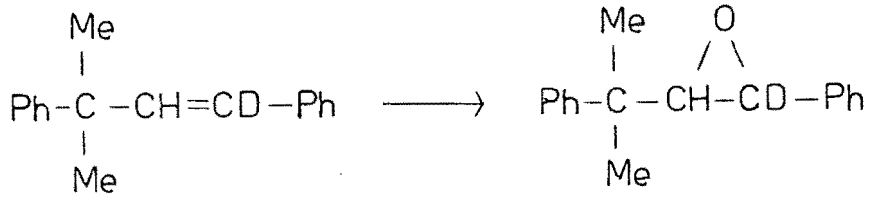


Scheme 75

(139a, 92a) were not detected in the reaction mixture. The aldehyde(140a) results from both C1-O and C2-O bond cleavage and to differentiate these possibilities *trans*-1-*d*-1,3-diphenyl-1,2-epoxy-3-methylbutane(190a) was prepared and its reaction with BF_3-etherate studied.

Reaction of *trans*-1-*d*-1,3-diphenyl-3-methylbut-1-ene (110a) with *m*-chloroperbenzoic acid gave *trans*-1-*d*-1,3-diphenyl-1,2-epoxy-3-methylbutane(190a). The presence of deuterium at

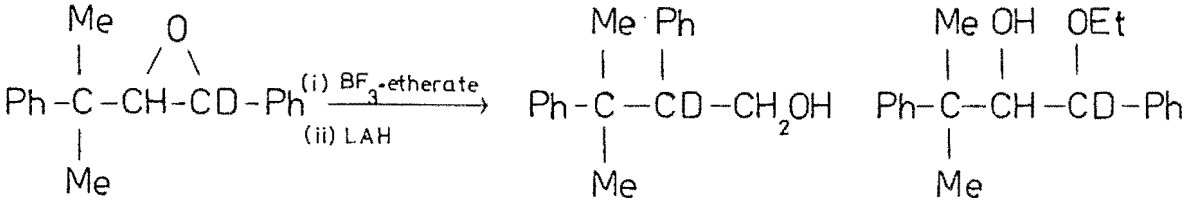
Cl was shown in its ^{1}Hn.m.r. spectrum by the loss of the H1 signal at δ_H3.73 and the absence of coupling with H2 which appeared as a singlet at δ_H3.05, broadened by coupling with deuterium. The ^{13}Cn.m.r. spectrum similarly showed the compound to be deuterated at C1 by a 1:1:1 triplet centered at δ_C55.8.



(110a) (190a)

trans-1-*d*-1,3-Diphenyl-1,2-epoxy-3-methylbutane(190a) was reacted with BF_3-etherate in benzene. The ^{1}Hn.m.r. spectrum of the crude reaction product showed the presence of the aldehyde proton resonance(δ_H9.80). The signals due to H2 of the ethoxy alcohol(189a) and H2 of the aldehyde were coincident and it was therefore necessary to separate the products to determine the extent of deuteration at C2 of the aldehyde. To prevent loss of deuterium from the deutero-aldehyde(193a) and in particular loss of any deuterium α to the carbonyl, by proton exchange on the alumina column, the crude reaction product was reduced with lithium aluminium hydride. The aldehyde gave deuterated 2,3-diphenyl-3-methyl-butan-1-ol(191a) which was separated by column chromotography from 1-*d*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(192a). The primary alcohol formed by the reduction of the deuterated aldehyde(193a) was identified by its spectral data to be 2-*d*-2,3-diphenyl-3-methylbutan-1-ol(191a). The ^{1}Hn.m.r. spectrum showed that deuterium was present only at C2 as the signal at δ_H3.08 in the spectrum of the undeuterated alcohol(153a)

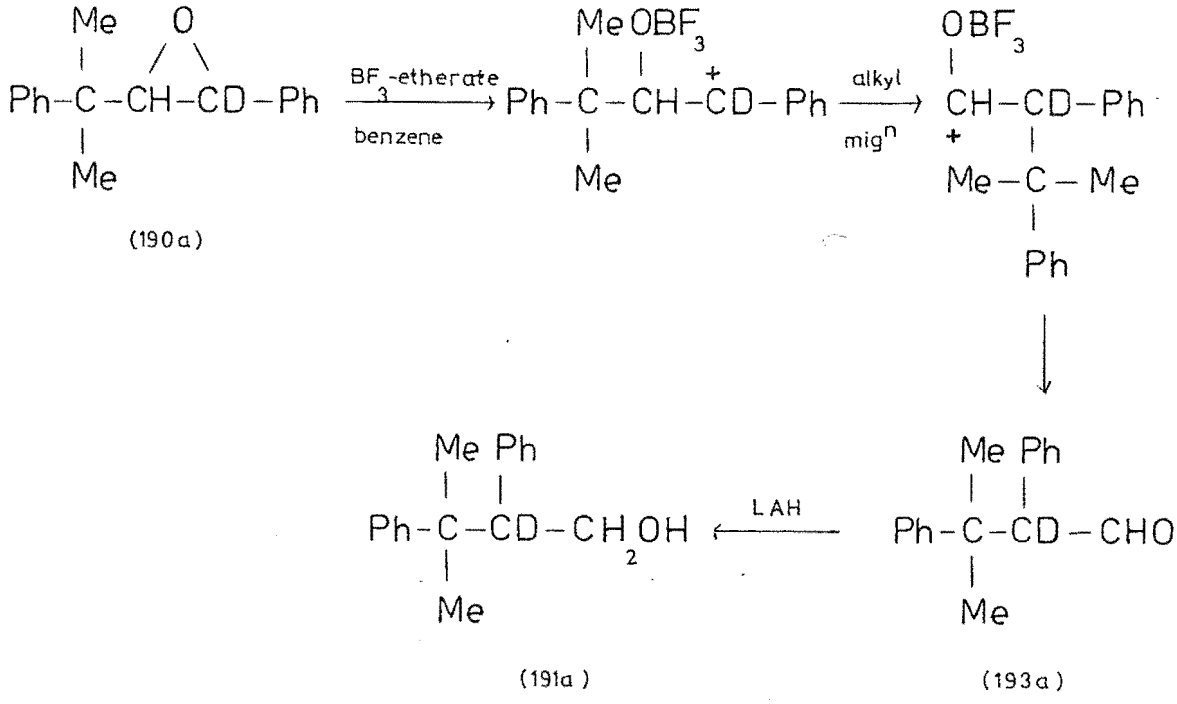
was absent. The C1 protons appeared as an AB quartet



(190a) (191a) (192a)

(δ_H3.84, 3.68, J 12Hz). The ^{13}Cn.m.r. spectrum showed that deuterium was present only at the C2 position. The signal expected at δ_C59.4(C2) was a 1:1:1 multiplet and the peak at δ_C62.5 remained a singlet showing 1-*d*-1,3-diphenyl-3-methyl-butan-1-ol(194a) was absent.

The presence of deuterium at C2 in the alcohol(191a) and hence at C2 in the precursor aldehyde(193a) demonstrates that the aldehyde(140a) is formed by C1-O cleavage followed by alkyl migration(Scheme 76). The direction of epoxide ring

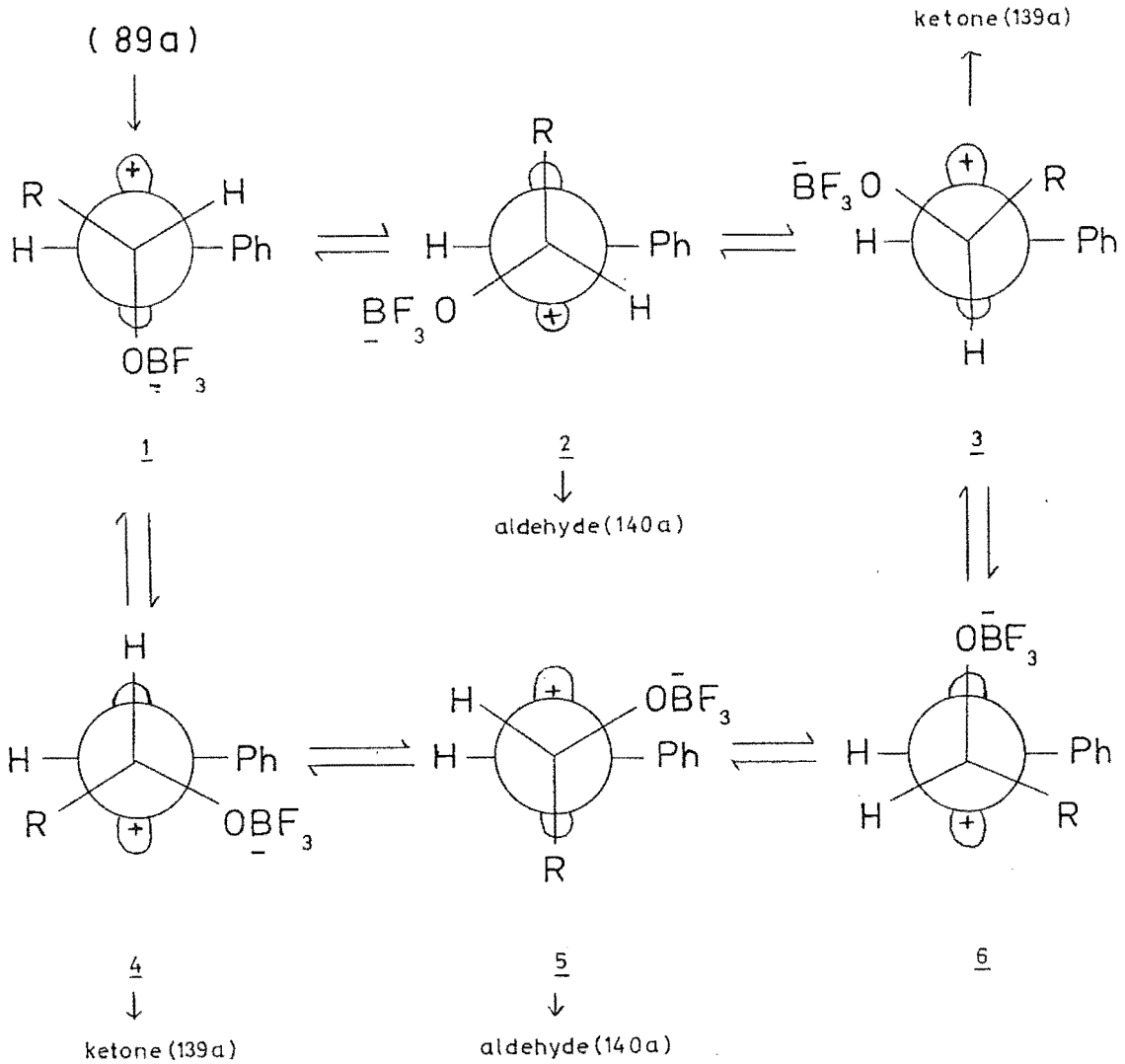


(190a) (191a) (193a)

Scheme 76

opening is dependent on the relative stability of the resulting cationic center and the stability of such cations will be affected by the substituent.

For C1-O cleavage the inherent 'migratory aptitude' of groups will play a role in determining the course of further reaction. Migratory aptitude is generally believed to follow the trend : aryl > acyl > H > alkyl[88]. Reaction of the epoxide(89a) with BF_3-etherate and C1-O bond cleavage gives the carbocation *1* (Scheme 77). Rotation about the



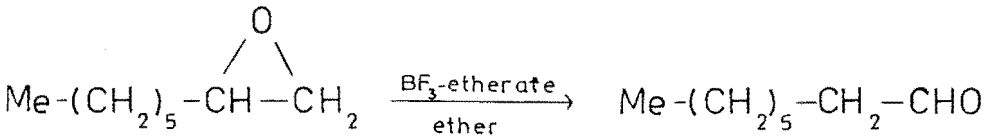
Scheme 77

central C1-C2 bond can occur to relieve the interaction of the phenyl ring and the solvated OBF_3 group to give conformer *2* in which interaction between the phenyl and alkyl groups is

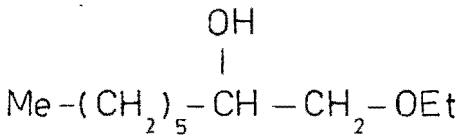
increased. In this conformer, *2*, the alkyl group is favourably aligned with the vacant p orbital for migration to occur. Further rotation to conformer *3* is hindered by interaction of the alkyl and phenyl groups and so the carbocation may not adopt a conformation from which hydrogen migration and ketone formation can occur. Rotation about the C1-C2 bond in the opposite direction to conformer *4* relieves the interaction between the alkyl and phenyl groups but increases interaction of the aromatic ring and the OBF_3 group. This interaction hinders the rotation to conformer *4* and therefore disfavours the alignment of the hydrogen with the electron deficient orbital and the possibility of ketone formation. The reaction mechanism for the rearrangement of the epoxide(89a) involves a cationic intermediate for which the rate of migration exceeds the rate of conformational change as rotation about the C1-C2 bond is hindered by the bulk of the substituents.

The formation of an ethanoxy alcohol product during a BF_3-etherate catalysed rearrangement of an epoxide is unusual and has been previously noted only for the reaction of 1,2-epoxyoctane(178) with BF_3-etherate and furthermore only when ether was used as the reaction medium. Kolaczinski[104] was able to detect both 1-ethanoxyoctan-2-ol(188) and 2-ethanoxy-octan-1-ol(195) in addition to the expected aldehyde product(179). Lim[105] isolated only 1-ethanoxyoctan-2-ol(188) in 60% yield and octanal(179) in 12% yield from the reaction mixture.

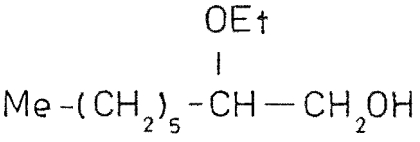
The structure of the ethanoxy alcohol(189a) formed by reaction of *trans*-1,3-diphenyl-3-methylbutane(89a) with BF_3-etherate in benzene was determined from its i.r. spectrum which showed the presence of an hydroxyl group(ν 3575 cm^{-1}) and absorptions(ν 1065, 1090, 110 cm^{-1}) indicative of an ether bond.



(178) (179)

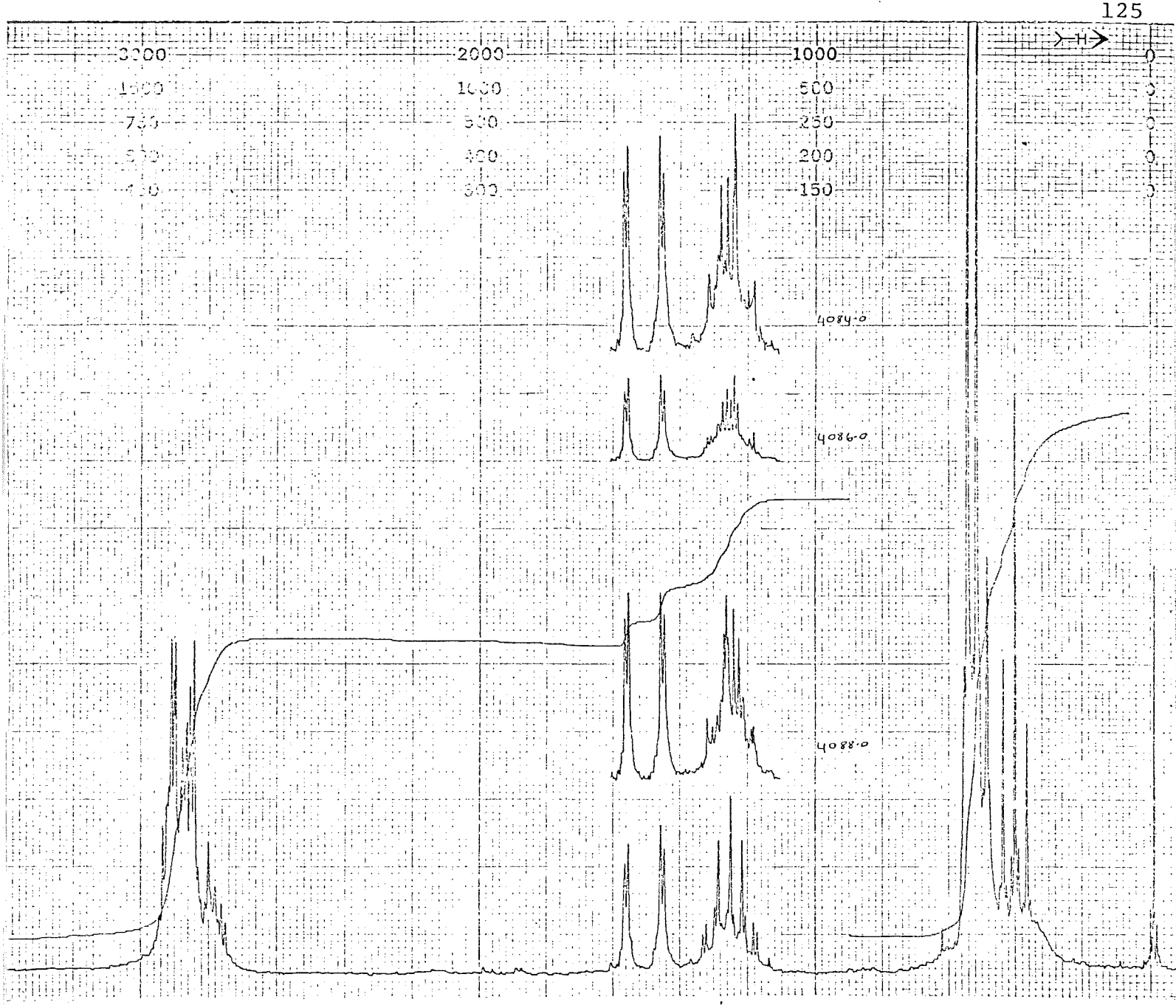


(188)

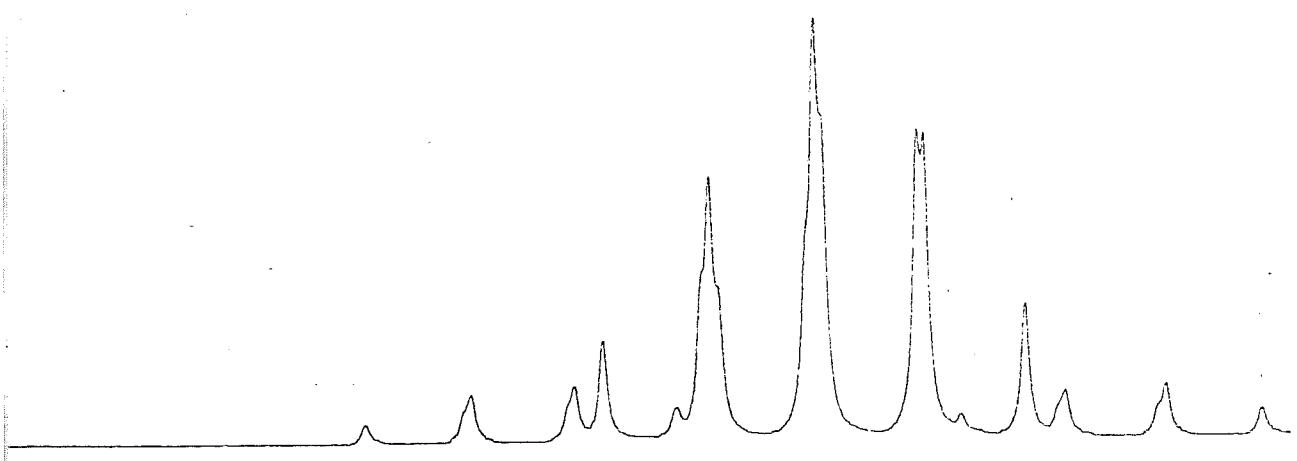


(195)

The ^{1}Hn.m.r. spectrum showed the presence of two singlet methyl peaks(δ_H1.35, 1.40) and two phenyl groups(δ_H7.18,Wh/2 11Hz). The presence of the ethoxy group was shown by a methyl triplet(δ_H1.03, J 7Hz) and methylene multiplet(δ_H3.15, Wh/2 17Hz). Irradiation of the methyl group(δ_H1.03) simplified the methylene multiplet to a poorly resolved AB quartet (δ_H3.22, 3.09, J 12Hz). The methylene protons of the ethoxy group are prochiral and therefore exhibit ABX_3 coupling rather than the more common A_2X_3 coupling. The second order multiplet observed for the methylene protons could be simulated using the following parameters: A, 170Hz; B, 185Hz; X, 60Hz, J_{AB} 14Hz, J_{AX} 6Hz, J_{BX} 6Hz (see diagrams). The coupling constants used in this simulation are as expected for this methylene system, thus providing further support for the structure. The ^{1}Hn.m.r. spectrum of (189a) further showed the presence of two methine hydrogens, one of which appeared as a doublet(δ_H3.90, J 2Hz) while the other was a broad



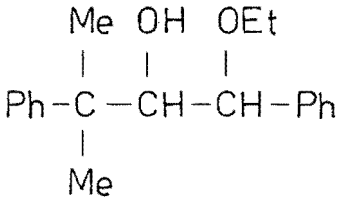
^{1}Hn.m.r. spectrum of 1R*, 2R*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(189a).



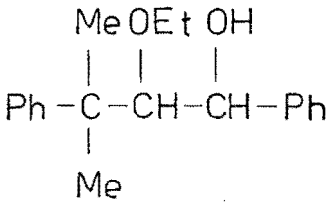
Simulated ^{1}Hn.m.r. spectrum for the ABX_3 system described above.

singlet(δ_H3.94, Wh/2 6Hz). On addition of D_2O to the sample, the latter signal appeared as a doublet(δ_H3.64, J 2Hz) indicating coupling between the hydrogen and the hydroxyl proton. The ^{13}Cn.m.r. spectrum showed the presence of two methyl peaks (δ_C22.5, 27.1) and signals for the ethoxy group(δ_C15.1, Me; δ_C63.9, CH_2). Seven aromatic signals were observed(δ_C147.1, 141.5, 128.2, 128.1, 127.4, 126.6, 126.0). The signal for the quaternary carbon C3 appeared at δ_C42.7 and the resonances for the neighbouring methine carbons were observed at δ_C79.4 and δ_C82.4.

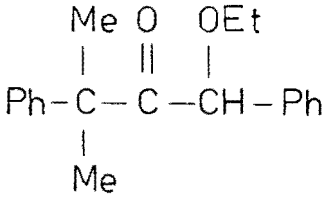
These data did not differentiate between the structures (189a) and (196). Oxidation of the ethanoxy alcohol afforded



(189a)



(196)

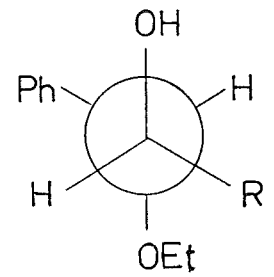


(197)

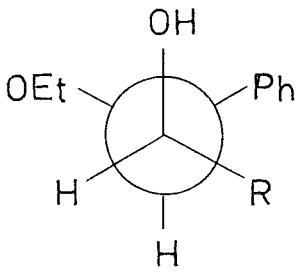
a non-conjugated ketone, ν 1715 cm^{-1} and λ 217nm(ε 27613), 253.5(2452), 259.5(2581), 265.5(2258), determining the structure as (197) and hence the ethanoxy alcohol as (189a). The ^{1}Hn.m.r. spectrum of the ketone(197) showed the presence of two methyl groups as singlet peaks(δ_H1.35, 1.55) and ten aromatic hydrogens as a narrow multiplet(δ_H7.15, Wh/2 2Hz). The resonances for the ethoxy group appeared at δ_H1.00, J 7Hz (Me) and δ_H3.19, 2.99, J 7Hz(CH_2) and the C1 proton appeared as a singlet(δ_H4.76). The structure of the ethanoxy alcohol(189a)

was further confirmed when the reaction was effected on the deutero-epoxide(190a) since the ^{1}Hn.m.r. spectrum of the product(192a) showed deuterium at C1 by the absence of the signal at δ_H3.90.

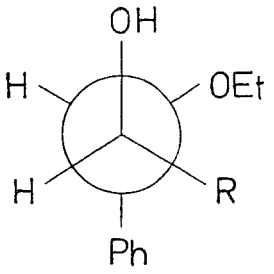
Having established the structure of the ethanoxy alcohol it remained to determine the relative configuration at the chiral C1 and C2 centers. Newman projections for the two possible configurations of the alcohol are shown in Scheme 78. For the R*S* structure the prefered rotational conformer would be A while for the R*R* structure, conformer D would be the more favoured because in these conformers the interaction of the bulky alkyl and phenyl groups is minimised. The observed



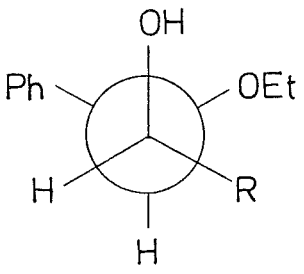
A



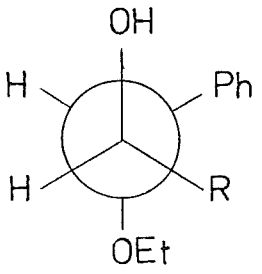
B



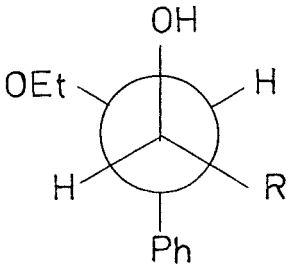
C R*S*



D



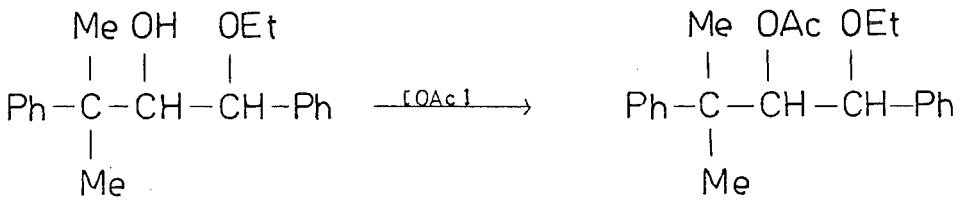
E



F R*R*

Scheme 78

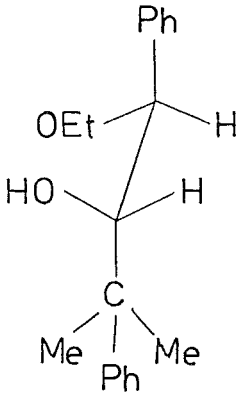
H1-H2 coupling constant of J = 2Hz is consistent with an average dihedral angle of c.60° [106] which is consistent with the ethanoxy alcohol being R*R* with conformer D favoured. While H1 and H2 of conformers B and C have a dihedral angle of 60°, the hydroxyl and ethoxy groups are positioned for intramolecular hydrogen bonding and hold the alkyl and phenyl groups in strained proximate positions. In the absence of hydrogen bonding, rotation about the C1-C2 bond would occur to give conformer A which would exhibit a larger H1-H2 coupling (c. J = 8Hz). To eliminate the possible influence of intramolecular hydrogen bonding on the conformation, the ethanoxy alcohol(189a) was acetylated. 1,3-Diphenyl-1-ethanoxy-3-methylbutyl-2-acetate(198) was identified from its ^{1}Hn.m.r. spectrum and showed only a small increase in the H1-H2 coupling (J = 2.5Hz). Clearly hydrogen bonding is not important in influencing the conformation and the ethanoxy alcohol(189a) can be established as having an R*R* configuration. This product must result from reaction involving retention of configuration at C1.



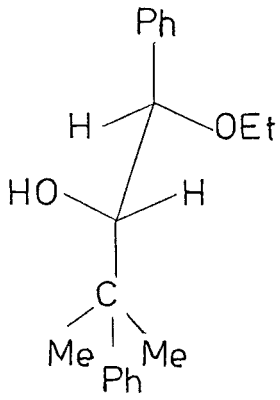
(189a) (198)

The R*S* stereoisomer was prepared by reaction of the epoxide(89a) with ethoxide, in a reaction for which good precedent exists for the attack by the nucleophile to occur with inversion of configuration[98]. The non-identity of this product(199) with that obtained from the BF_3-etherate catalysed

reaction confirms the configuration of the ethanoxy alcohol (189a) obtained from that reaction. Reaction of epoxide(89a) with sodium ethoxide in ethanol yielded a single ethanoxy alcohol product(199). Its ^{1}Hn.m.r. spectrum showed the presence of the three methyl groups, two singlet peaks(δ_H1.30, 1.43) and one triplet signal(δ_H1.00, J 7Hz) which was coupled to a methylene multiplet(δ_H3.07, Wh/2 15Hz). The ten aromatic protons appeared as a narrow multiplet(δ_H7.25, Wh/2 2Hz) and the hydroxyl proton peak was masked by a methyl signal at δ_H1.43. The C1 and C2 protons appeared as an AB quartet(δ_H3.92, 3.86, J 7Hz), in contrast with the signals observed for H1 and H2 for the R*R* isomer(189a)(δ_H3.64,3.90, J 2Hz). The acetate(200) formed from the ethanoxy alcohol(199)



(189a)

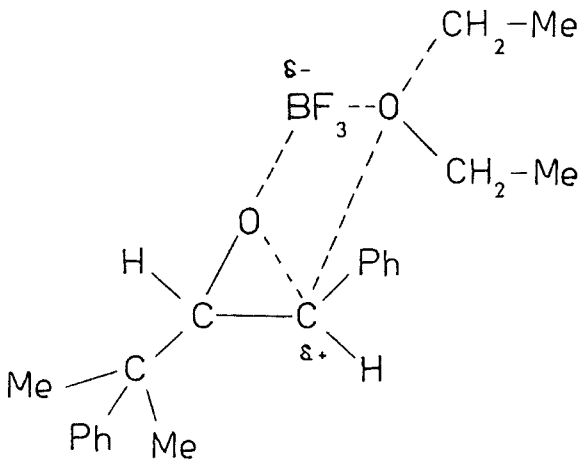


(199)

showed a large H1-H2 coupling constant of J = 8Hz, suggesting that the molecule exists in conformer A(Scheme 78). Oxidation of the R*S* ethanoxy alcohol(199) yielded the ethanoxy ketone(197) identical in all respects with that obtained by oxidation of R*R* ethanoxy alcohol(189a).

Since this reaction of the epoxide, 1,3-diphenyl-1, 2-epoxy-3-methylbutane(89a) with BF_3-etherate was carried out in benzene, the source of the nucleophile for the

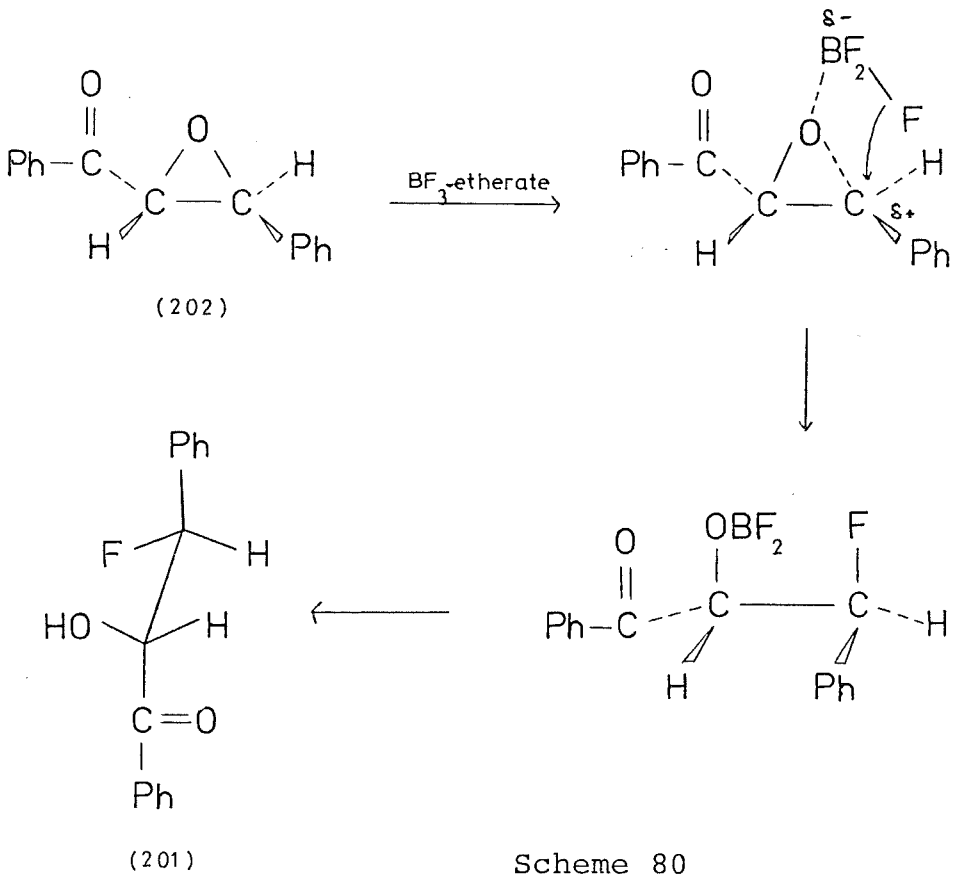
formation of 1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(189a) can therefore be presumed to be an ether molecule coordinated to BF_3-etherate. Since attack at C1 is *syn* with respect to the epoxide ring, the ethoxide nucleophile is presumed to be associated with the BF_3-etherate molecule coordinated to the epoxide oxygen. The transition state required for such a reaction(Scheme 79) is not too dissimilar from that suggested by House[107] for the formation of the *cis*-fluorohydrin(201). House proposed an ion pair mechanism



Scheme 79

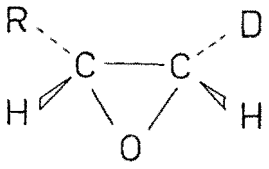
to explain the formation of the *cis*-fluorohydrin on treating *trans*-benzalacetophenone oxide(202) with BF_3-etherate(Scheme 80).

Ethoxide attack during epoxide cleavage reactions catalysed by BF_3-etherate was first reported by Kolaczinski[104] who identified 1-ethanoxyoctan-2-ol(188) and 2-ethanoxyoctan-1-ol(195) as products in the BF_3-etherate reaction of 1,2-epoxyoctane(178) in ether. He suggested the reaction involved the production of a primary cation intermediate of sufficient reactivity to cleave diethyl ether. Lim[105] repeated this reaction and observed the formation of 1-ethanoxyoctan-2-ol(188) but not 2-ethanoxyoctan-1-ol(195). Octanal(179)

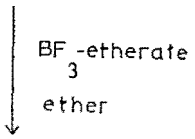


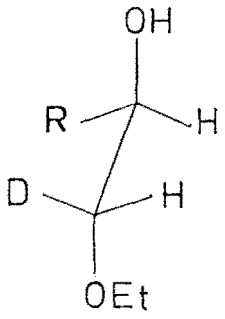
Scheme 80

was also formed. It was suggested that the ethanoxy alcohol(188) was formed by nucleophilic attack at the less hindered C1 position by solvent ether. Lim studied the stereochemistry of the reaction by examination of the mono- and di-deuterated epoxides. He found that the reaction of 1R*,2R*-1-*d*-1,2-epoxyoctane(203) with BF_3-etherate in ether gave 1R*,2R*-1-*d*-1-ethanoxyoctan-2-ol(204) and 1R*,2S*-1,2-dideutero-1,2-epoxyoctane(205) reacted to give 1R*,2S*-1,2-dideutero-1-ethanoxyoctan-2-ol(206), the identities of which were established by comparison with the products obtained by reaction of the epoxyoctanes with sodium ethoxide in ethanol. In each case the product was formed with inversion of configuration at C1. It should be noted that the ethanoxy alcohol (189a) produced by reaction of BF_3-etherate with 1,3-diphenyl-1,2-epoxy-3-methylbutane(89a) is formed with retention of configuration at C1.

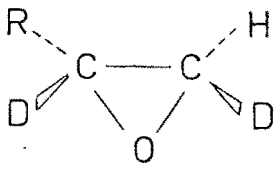


(203)

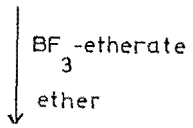


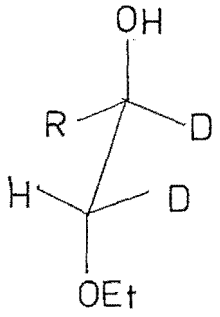


(204)



(205)



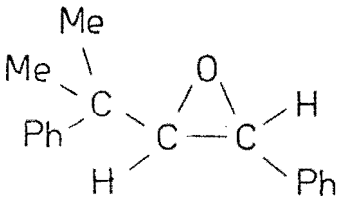


(206)

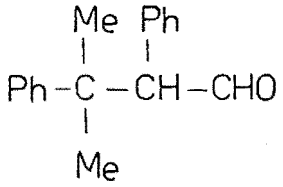
(b) Rearrangement of *trans*-1,3-Diphenyl-1,2-epoxy-3-methyl-3-phenylbutane(89a) with BF_3-etherate in Ether.

Previous studies on the BF_3-etherate catalysed rearrangement of epoxides have shown that a change in solvent from benzene to ether may alter product distribution[103], the mechanism by which products are formed[108] and even the type of product formed[97,109]. These differences may accommodate the lower electrophilicity of BF_3-etherate in ether compared with that in benzene and this is seen by a reduction in the rate of reaction. Benzene is perhaps a solvent more capable of stabilising intermediate carbocation than ether. A reasonable estimate of this ability can be obtained from the S-values calculated by Brownstein[110] :- benzene, -0.215; ether, -0.277. These values are related to solvent polarity relative to ethanol. The more negative the value the less polar the solvent.

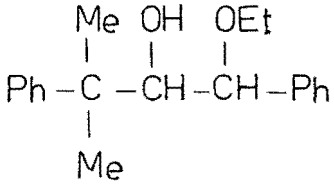
Previous studies have shown that a change in the reaction medium from benzene to ether in a BF_3-etherate catalysed reaction has an effect on the products formed. Reaction of epoxide(89a) with BF_3-etherate in ether was therefore investigated. Reaction for 24hr gave the following products: 2,3-diphenyl-3-methylbutanal(140a)(26%), 1R*,2R*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(189a)(15%), 1,3-diphenyl-3-methylbutan-2-one(139a)(6%), *E* and *Z*-2,3-diphenyl-1-ethanoxy-3-methylbut-1-ene(207a)(23%) and di-(1R*,2R*-1,3-diphenyl-2-hydroxy-3-methylbutane)ether(208a)(2%).



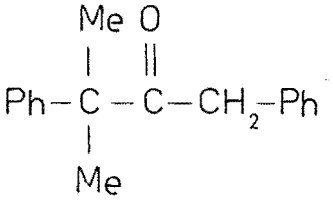
(89a)



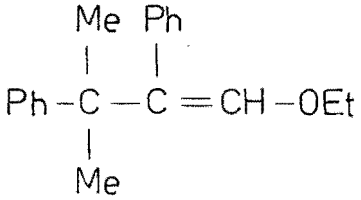
(140a)(26%)



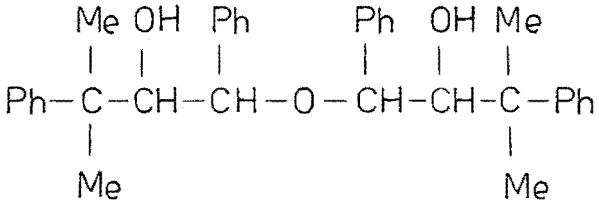
(189a)(15%)



(139a)(6%)



(207a)(23%)



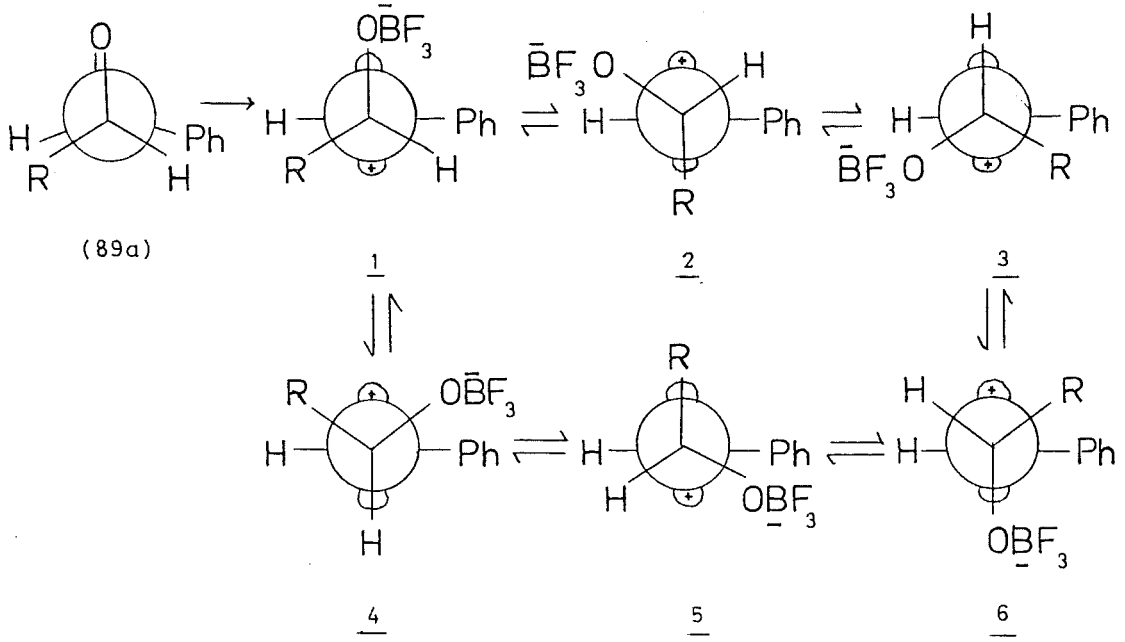
(208a)(2%)

The aldehyde(140a) was identified by comparison with an authentic sample formed by the reaction of the epoxide(89a) with BF_3-etherate in benzene. Reaction of the deuterated epoxide(190d) in ether afforded aldehyde with deuterium at C2 showing that, as in benzene, the reaction involved C1-O bond cleavage and alkyl group migration. The 1R*, 2R* - ethanoxy alcohol(189a) was identical to the sample obtained from the reaction of the epoxide(89a) in benzene. 1R*,2S*- ethanoxy alcohol(199) could not be detected in the reaction mixture. Again, the ethanoxy alcohol is formed with retention of configuration at C1 and this could be taken as evidence that attack by ether occurs from the BF_3 coordinated molecule.

The infrared spectrum of the ketone(139a) showed carbonyl absorption, ν 1715 cm^{-1}, which indicated that the carbonyl group was not conjugated to the aromatic ring and this was confirmed by the ultraviolet spectrum, λ 212.5nm (ε 7143), 253.5(417). The ^{1}Hn.m.r. spectrum of the ketone(139a) showed a singlet peak(δ_H1.50) due to two methyl groups, a singlet(δ_H3.48), deshielded by the neighbouring carbonyl group, due to the Cl methylene protons and a narrow multiplet(δ_H7.10, Wh/2 5Hz) due to the two aromatic rings. The structure of (139a) was confirmed by the ^{13}Cn.m.r. spectrum which showed the resonances for a quaternary carbon(δ_C52.8) deshielded by the neighbouring carbonyl group(δ_C209.8). The methyl carbons signal appeared at δ_C25.0 and the methylene carbon peak at δ_C44.1. The aromatic carbons were represented by eight peaks (ClAr:δ_C135.0, 129.4, 128.2, 126.5; C3Ar: δ_C143.6, 126.3, 128.9, 127.1).

The ketone(139a) results from Cl-O bond cleavage followed by hydrogen migration. In the reaction of the epoxide(89a) with BF_3-etherate in benzene, the absence of ketone formation(6% formed in ether) may be due to steric effects preventing the alignment of the hydrogen with the electron deficient orbital. The two conformers *3* and *4* (Scheme 81), in which hydrogen is favourably aligned for migration, involve increased interaction between the bulky alkyl group or solvated OBF_3 group and the phenyl ring. In the slower reaction in ether hydrogen migration becomes competitive with alkyl migration.

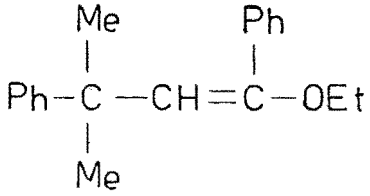
The structure of the vinyl ethers(207a) was established in the following manner. The isomers were formed in the ratio 5:1. It was not possible to isolate sufficient of the minor isomer to obtain full spectral data for that isomer.



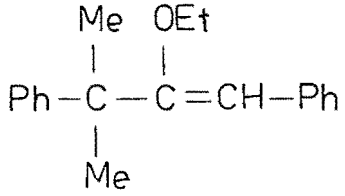
Scheme 81

The ^{1}Hn.m.r. spectrum of the major isomer(207a) showed the resonances for an ethoxy group(δ_H1.12, t, J 7Hz, Me; δ_H3.74, 3.56, J 7Hz, CH_2) and for a single vinyl proton (δ_H6.03). Two methyl groups appeared as a single peak at δ_H1.35 and a broad multiplet centered at δ_H6.90(Wh/2 21Hz) was due to ten aromatic protons. The ^{13}Cn.m.r. spectrum showed the signals for the ethoxy group(δ_C15.2, Me: δ_C67.7,CH_2), for the methyl carbons(δ_C29.2), for a quaternary carbon(δ_C41.6) and for two phenyl rings(δ_C148.4, 138.0, 130.0, 127.9, 127.2, 126.7, 126.0, 125.6). A vinyl carbon peak which the sford spectrum showed to be a doublet, appeared at δ142.5. The other vinyl carbon signal was not observed and was assumed to be masked by the aromatic carbons.

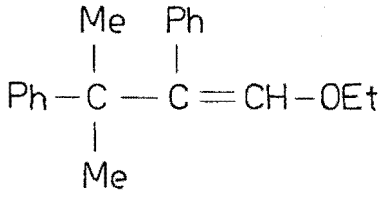
The spectral data did not differentiate between three possible structural isomers of the vinyl ether(Scheme 82) and in order to determine the structure reaction of the 5:1 mixture of the vinyl ether(207) with dilute hydrochloric acid was effected. 2,3-Diphenyl-3-methylbutanal(140a) was the sole



1



2



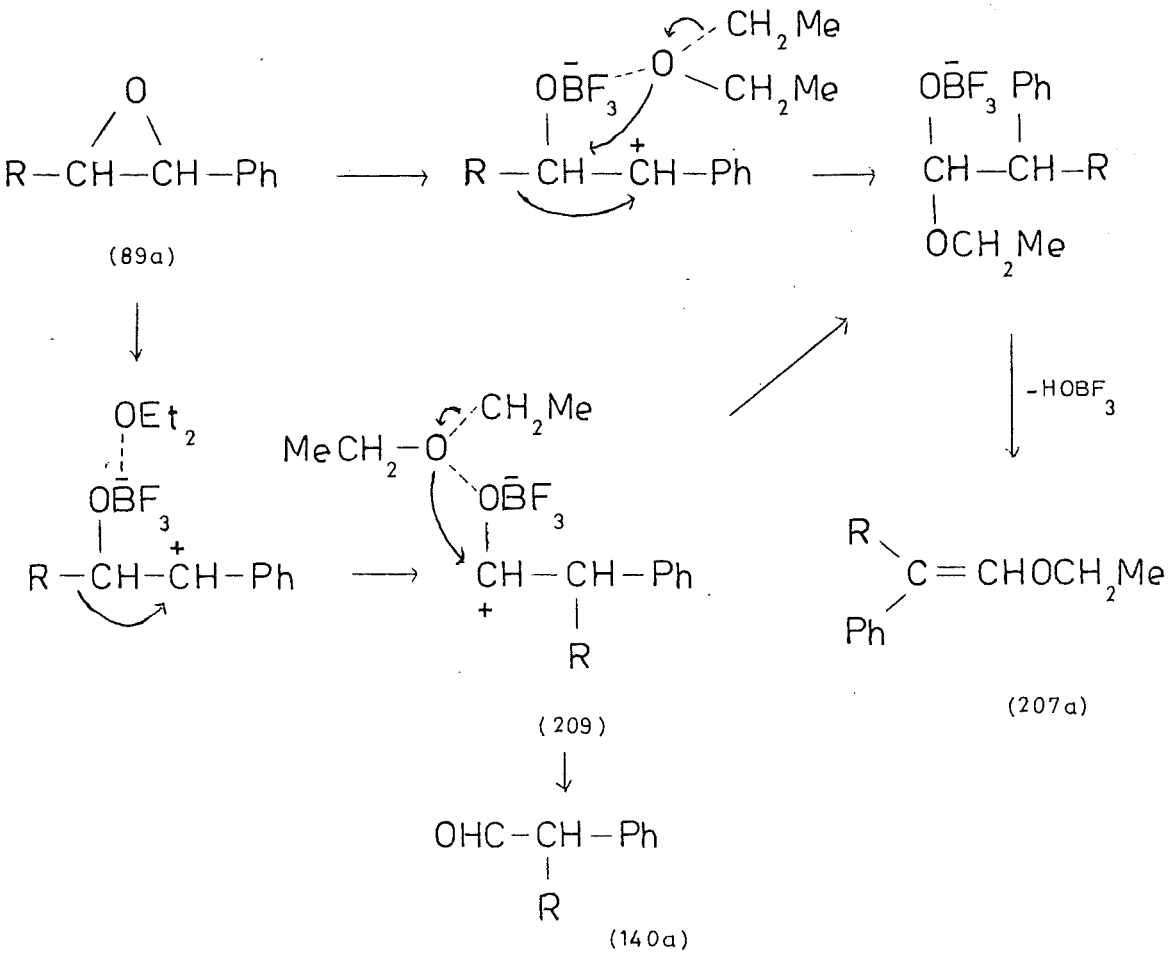
3

Scheme 82

product which indicated that 2,3-diphenyl-1-ethanoxy-3-methyl-but-1-ene(isomer *3*) was the precursor vinyl ether(207). ^{1}Hn.m.r. Eu(fod)$_3$ studies on the mixture of isomers showed that the vinyl proton of the major isomer was more sensitive to the addition of the shift reagent but did not allow the differentiation of the geometric isomers.

Reaction of the deuterated epoxide(190d) with BF_3-etherate in ether gave vinyl ethers(207d) that were found by ^{1}Hn.m.r. spectroscopy to contain no deuterium.2,3-Diphenyl-1-ethanoxy-3-methylbut-1-ene(207a) is envisaged as being formed by initial Cl-O bond cleavage followed by alkyl migration. The intermediate cation(209) can collapse to the aldehyde(140a) and would exist in equilibrium with the aldehyde. Failure to detect vinyl ether products(207) on the addition of BF_3-etherate to the aldehyde(140a), exclude the cation(209) as an intermediate in the formation of(207). It must therefore be concluded that the ethoxy group is bound before the rearrangement to the aldehyde is complete and possibly as the alkyl group migrates(Scheme 83).

Further investigation concerning the mechanism of formation of the vinyl ethers was not pursued since their



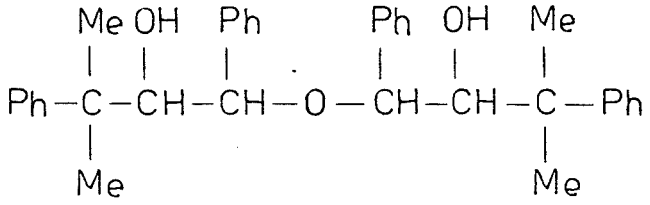
Scheme 83

formation was found to be dependent on the batch of BF_3-etherate being used even though the reagent was distilled several times immediately prior to use for all experiments.

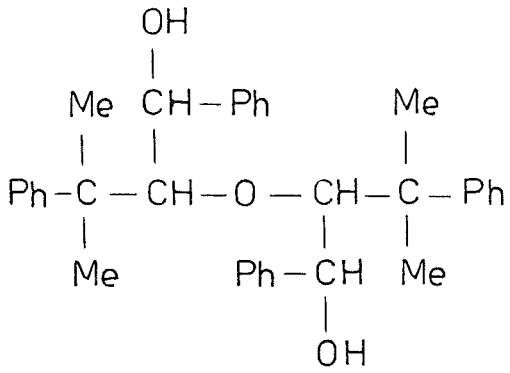
The ^{1}Hn.m.r. spectrum of di-(1,3-diphenyl-3-methyl-2-hydroxybutane)ether(208a) showed the signals for two methyl groups(δ_H1.32, 1.41), for a hydroxyl proton(δ_H2.58), which was removed on addition of D_2O, and for aromatic protons which appeared as a wide multiplet centered at δ_H7.17(Wh/2 10Hz). Neighbouring methine protons, deshielded by the proximity of electronegative groups, appeared as an AB quartet(δ_H4.03, 4.73, J 35Hz). The ^{13}Cn.m.r. spectrum showed resonances for two methyl carbons(δ_C22.7, 27.3), a quarternary carbon (δ_C43.2), two phenyl rings(δ_C146.1, 140.9, 128.3, 128.2, 128.0, 127.2, 126.5, 126.4) and for two methine carbons(δ_C81.2, 65.6). The infrared spectrum showed the presence of a

C-O-C stretch(ν 1070 cm^{-1}) and a hydroxyl group(ν 3570 cm^{-1}). This data is consistent with the compound being a symmetrical dimer.

Of the three possible structures(Scheme 84) the hemiacetal, *3*, may be eliminated since the compound would not be stable to acid. Structures *1* and *2* can be differentiated by oxidation as *1* will give rise to an unconjugated ketone(210) whereas *2* will form an aryl conjugated ketone(211). Oxidation of the ether(208a) gave an unconjugated ketone(210), i.r. ν 1725 cm^{-1}; u.v.λ 209.5 nm(ε 25257). The structure of the oxidation product(210) was determined from its ^{1}Hn.m.r. and



1



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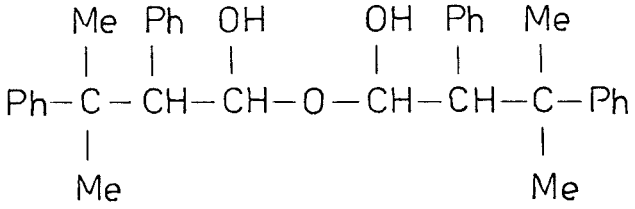
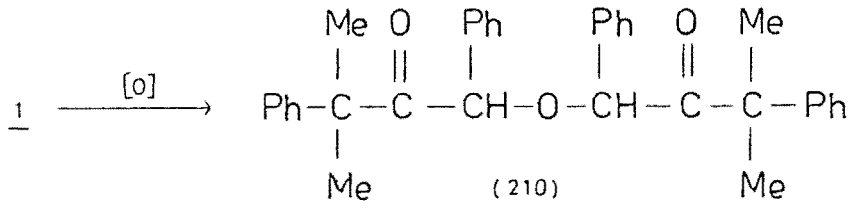
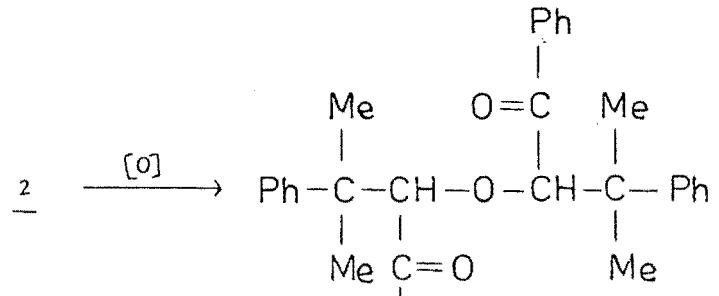


3

Scheme 84



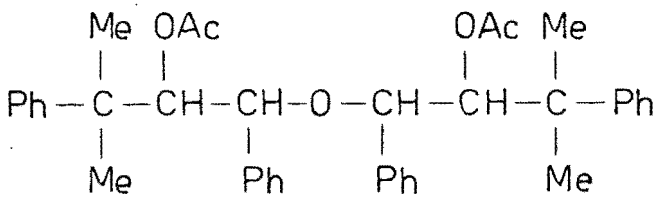
(210)



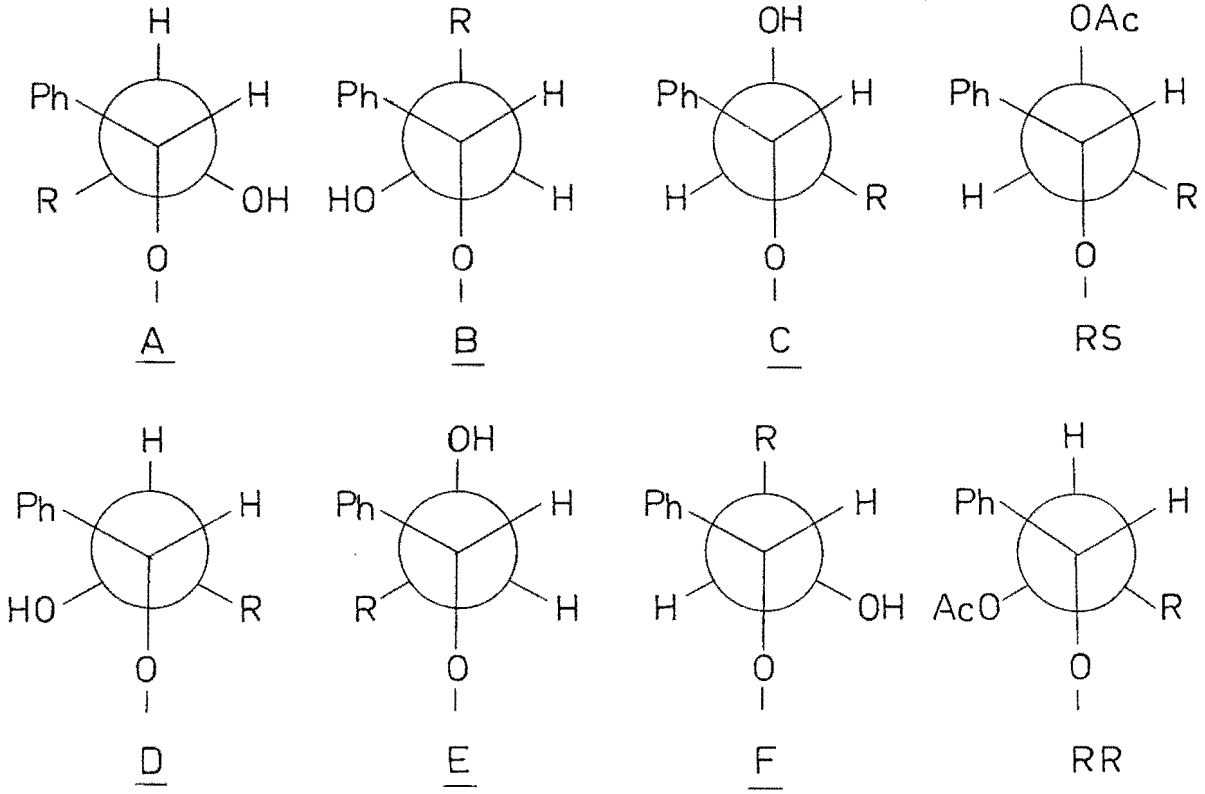
(211)

^{13}Cn.m.r. spectra. The ^{1}Hn.m.r. spectrum showed the signals for two methyl groups(δ_H1.38, 1.62), for aromatic protons (δ_H7.18, Wh/2 8Hz) and a single methine proton(δ_H5.27) deshielded by the carbonyl and ether moieties. The ^{13}Cn.m.r. spectrum showed resonances for the methyl carbons(δ_C25.1), for a quaternary carbon(δ_C52.8), a methine carbon(δ_C58.3), a carbonyl carbon(δ_C204.7) and for the aromatic carbons(δ_C141.4, 136.0, 128.8, 128.7, 128.3, 127.4, 126.7).

The ^{1}Hn.m.r. spectrum of the ether(208a) showed H1-H2 coupling of J = 3.5Hz indicating an average dihedral angle of about 60^{o}[106]. On acetylation of the ether(208a) to (212), the H1-H2 coupling constant increased to J = 7.5Hz. Examination of the Newman projections of the ether(208a)(Scheme 85) show that conformers *A*, *B*, *D* and *E* hold H1 and H2 at a dihedral angle of approximately 60^{o} and satisfy the observed coupling constant, J = 3.5Hz. The increase in the H1-H2 coupling constant(J = 7.5Hz) on acetylation implies that rotation about the C1-C2 bond has occurred as a result of the removal of hydrogen bonding. Rotation of this nature, relieving the steric interactions between the phenyl and alkyl groups, would occur only for conformers *A* and *B*. The configuration(RS) at C1 and C2 shows that inversion of



(212)

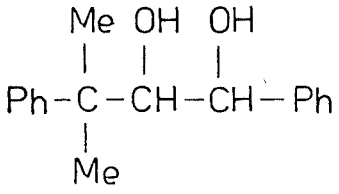


Scheme 85

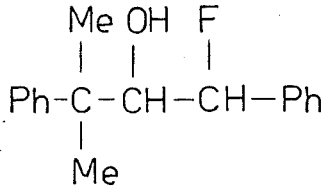
configuration has occurred at the C1 sites on the formation of the ether bond.

Formation of the ether(208a) requires the presence of water which may be provided by the formation of the vinyl ethers(207a). When the reaction of the epoxide(89a) was carried out with a batch of BF_3-etherate which did not give vinyl ethers(207a), dimer(208a) was also absent from the reaction product. Reaction of the epoxide(89a) with BF_3-etherate in ether to which a trace of water was added resulted in the formation of the dimer ether(208a)(c.14%) without the formation of the vinyl ethers(207a). This suggests that the

diol, 1,3-diphenyl-3-methylbutane-1,2-diol(213) might be involved in the reaction. Reaction of a mixture of diol(213),



(213)

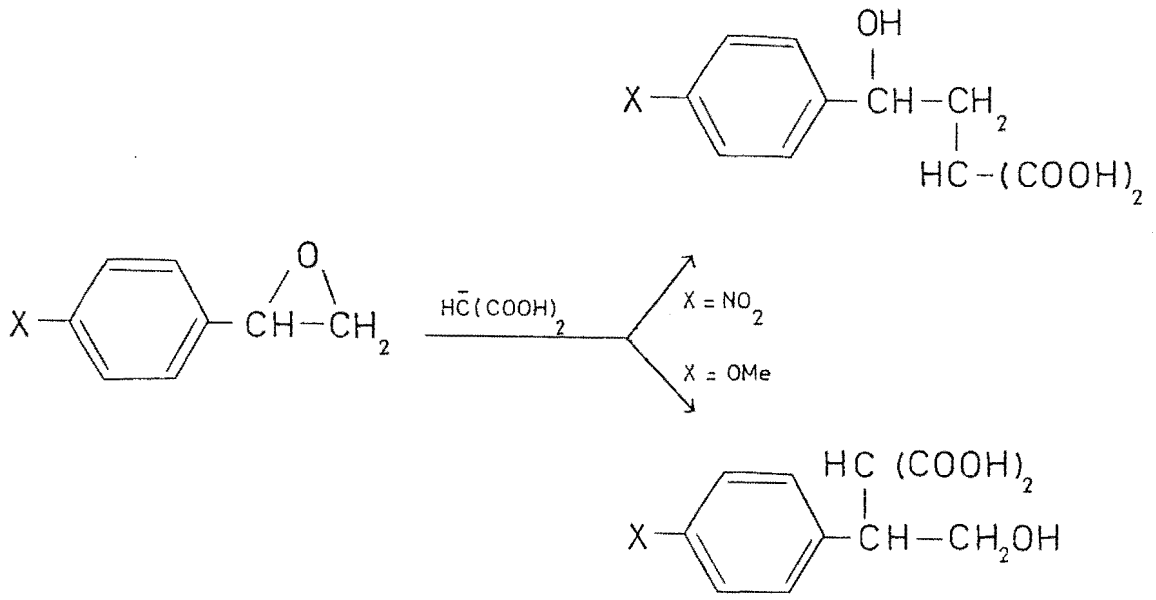


(214)

prepared by reaction of epoxide(89a) with aqueous perchloric acid, and epoxide(89a) with BF_3-etherate however gave no dimer(208a). While the mode of the formation of dimer(208a) remains unclear, the intermediacy of the diol(213) and/or fluorohydrin(214) cannot be excluded.

(c) Reaction of *trans*-1-Aryl-1,2-epoxy-3-methyl-3-phenylbutanes with BF_3-etherate.

The epoxide system was further examined by studying the effect of substituents on the C1 aromatic ring. Variations in the regioselectivity of nucleophilic attack have been observed for aryl substituted epoxides. The direction of ring opening for nucleophilic attack on styrene oxides by the malonate ion is strongly influenced by the substituent on the aromatic ring[111] (Scheme 86). The electron donating methoxy substituent promoted nucleophilic attack at the more highly substituted secondary carbon while the electron withdrawing nitro group favoured reaction at the terminal carbon. These results are in contrast with the common assumption that the effect of an electron donating substituent on the direction of

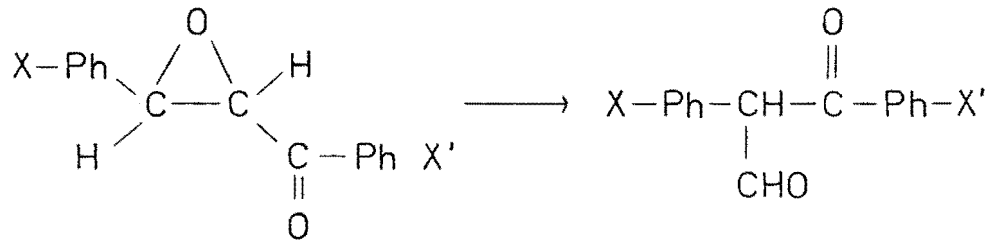


Scheme 86

S_N2 ring opening in epoxides is to favour attack at the primary carbon atom which is more disposed to accommodate a negative charge. Kayser and Morand[89] discuss these variations in terms of a hard-soft acid-base theory whereby coordination of the oxygen atom of the oxirane ring with a hard acid produces a 'pulling effect' which determines the direction of ring opening. In the absence of a strong 'pulling effect', the 'pushing effect' of the incoming nucleophile is more important.

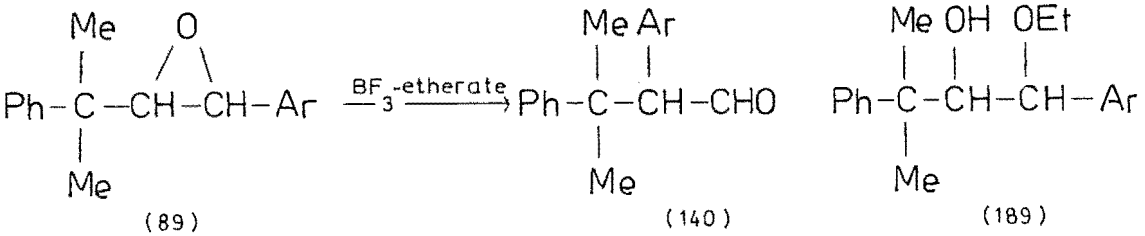
The BF_3-etherate catalysed conversion of *trans*-benzal-acetophenone oxide(202) to α-formyldesoxybenzoin(215) has been demonstrated to involve the intramolecular migration of a benzoyl group[112]. Electron donating substituents(X or X') have been found to enhance the rate of this rearrangement reaction while electron withdrawing substituents have the reverse effect[107].

The BF_3-etherate catalysed rearrangements of the Cl-aryl substituted epoxides(89b-f) were studied in the solvent benzene while those of (89b,d,e) were also effected in ether solution.



(202) (215)

The epoxides, *trans*-1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes(89b-f), were reacted with BF_3-etherate in benzene to give 2-aryl-3-methyl-3-phenylbutanals(140b-f) and 1R*,2R*-1-aryl-1-ethanoxy-3-methyl-3-phenylbutan-2-ols(189b-f).



(89) (140) (189)

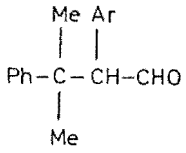
These products were identified by comparison of their spectral data with those of the phenyl substituted substrates. The yield of each compound was determined by the weight of material isolated after column chromotography(Table 5) and from the ^{1}Hn.m.r. spectrum of the crude reaction product. The values differ due to decomposition of the aldehyde on the column.

The aldehydes(140b-f) were identified from their infrared spectrum in which the carbonyl stretch appeared between ν 1715 cm^{-1} and ν 1725 cm^{-1} and the aldehyde proton stretch appeared at approximately ν 2720 cm^{-1}. The ^{1}Hn.m.r. spectra showed the aldehyde proton signals at around δ_H9.7, coupled (J ≈ 3Hz) to the H2 resonance which appeared at about δ_H3.7. The structure of the aldehydes(140b-f) was further confirmed by reduction to the primary alcohols, 2-aryl-3-methyl-3-phenylbutan-1-ols(153b-f), which were identified by comparison

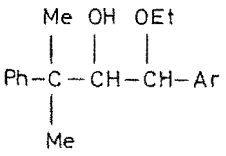
TABLE 5

Reaction of *trans*-1-Aryl-1,2-epoxy-3-methyl-3-phenylbutanes(89) with BF_3-etherate in Benzene.

% product isolated and (in brackets) the ratio of products determined by the ^{1}Hn.m.r. of the crude reaction product.

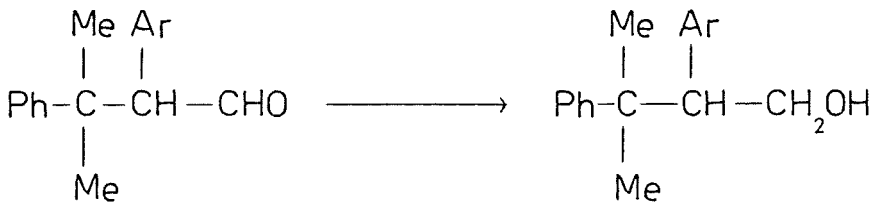


(140)



(189)

Ar		
p-Ph-OMe	51 (1.5)	34 (1)
p-Ph-Me	49 (2)	32 (1)
Ph	45 (4)	15 (1)
p-Ph-Cl	33 (5)	17 (1)
m-Ph-Cl	67 (20)	- (1)
3',4'-Ph-Cl_2	64 (9)	8 (1)



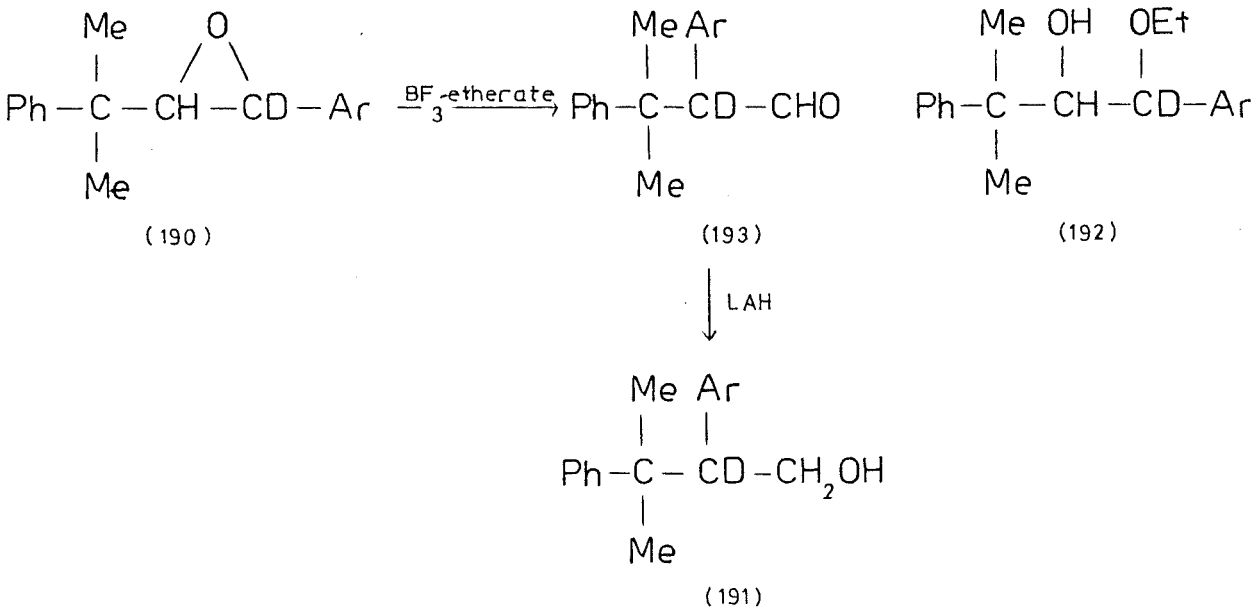
(140) (153)

of their spectra with those of the phenyl derivative(153a).

As described earlier, the aldehyde can be formed by C1-O bond cleavage followed by alkyl migration or C2-O bond cleavage followed by aryl migration. C1-O bond cleavage and alkyl migration occurred in the reaction of the phenyl epoxide(89a) with BF_3-etherate in benzene. In order to determine the effect that substitution on the C1 aryl group has on epoxide ring opening, the C1-deuterated epoxides(190b, *p*-Ph-OMe; d,*p*-Ph-Cl; e,*m*-Ph-Cl) were prepared.

The *trans*-1-*d*-1-aryl-3-methyl-3-phenylbut-1-enes(110b, d,e) reacted with *m*-chloroperbenzoic acid to give *trans*-1-*d*-1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes(190b,d,e). Deuteration at C1 was determined by ^{13}Cn.m.r. and ^{1}Hn.m.r. spectroscopy to be complete.

The deuterated epoxides(190b,d,e) reacted with BF_3-etherate in benzene to give deuterated aldehydes(193b,d,e) and 1-*d*-1-aryl-1-ethanoxy-3-methyl-3-phenylbutan-2-ols(192b,d,e). To enable separation of the products without loss of deuterium, the crude reaction mixture was reacted with lithium aluminium hydride, which reduced the aldehyde(193) to a primary alcohol (191) without affecting the ethoxy alcohol(192). The primary alcohols(191b,d,e) isolated were deuterated at C2 which showed that C1-O bond cleavage followed by alkyl migration occurs for epoxides(89b, *p*-Ph-OMe; d,*p*-Ph-Cl; e, *m*-Ph-Cl) and these substituents form a useful range.



Chloro substituents on the Cl aromatic ring will destabilise the cation formed at Cl on epoxide ring opening but the destabilising effect is not sufficient to induce C2-O bond cleavage. It is however sufficient to substantially reduce the formation of the ethanoxy alcohols(189). The ethanoxy alcohols(189b,c,d,f) were identified from their spectral data as described for the phenyl derivative(189a). The H1-H2 coupling was small($J \approx 2Hz$) for the alcohols(189b,c, d,f) which showed that these alcohols had the R*R* configuration and that ethanoxy group attack occurred with retention of configuration at the Cl position(p.124).

The ratio of aldehyde(140) to ethanoxy alcohol(189) produced in the BF_3-etherate catalysed ring opening of the series of substituted epoxides(89) was affected by the Cl aryl substituent. The *para*-methoxy substituent is electron donating and will stablise a cation formed at Cl. This is shown by the increased percentage of intermolecular attack by the ethanoxy group. The *meta*-chloro substituent is electron withdrawing and will destablise the cation formed at Cl. Intermolecular nucleophilic attack by the ethanoxy group does not now compete with alkyl migration.

As previously noted,a change in reaction medium from benzene to ether has an effect on the BF_3-etherate catalysed rearrangement of the epoxide(89a) in the formation of additional products. The reaction of the phenyl substituted epoxide(89a) with BF_3-etherate in ether gave, in addition to the aldehyde(140a) and ethanoxy alcohol(189a), a ketone(139a), a vinyl ether(207a) and a dimer ether(208a). To determine the effect that substituents on the Cl aromatic ring have on the formation of these products, epoxides(89b,*p*-Ph-OMe; d, *p*-Ph-Cl; e, *m*-Ph-Cl) were reacted with BF_3-etherate in ether. The yields of products, given in Table 6, were determined by the weights isolated. The yield of aldehyde(140) isolated was lower than determined from the crude reaction product due to decomposition on the column. The products isolated were identified by their ^{1}Hn.m.r., ^{13}Cn.m.r. and i.r. spectra and by comparison with the data available for the analogous phenyl derivatives.

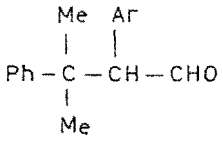
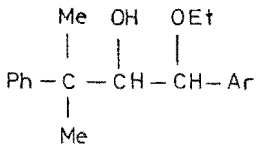
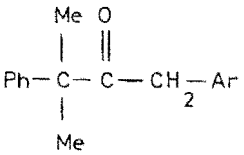
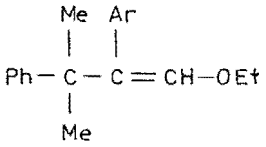
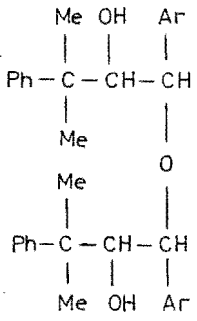
The 2-aryl-3-methyl-3-phenylbutanals(140b,d,e) were formed for each of the substituted epoxides(89b,d,e) by Cl-O bond cleavage followed by alkyl migration. In ether(cf benzene) nucleophilic attack and alternative reaction processes compete with alkyl migration with a resulting decrease in the amount of aldehyde formed. The 1R*,2R*-1-aryl-1-ethanoxy-3-methyl-3-phenylbutan-2-ols(189b,d) were formed from the *para*-methoxy and *para*-chloro substituted epoxides(89b,d). Ethanoxy alcohol(189e) was not formed however from reaction of the *meta*-chloro substituted epoxide(89e) with BF_3-etherate in ether or in benzene.

The 1-aryl-3-methyl-3-phenylbutan-2-ones(139b,d,e) were formed in the reactions of the substituted epoxides(89b,d,e) with BF_3-etherate in ether by Cl-O bond cleavage and hydrogen migration. The absence of ketone formation when the reaction

TABLE 6

Reaction of *trans*-1-Aryl-1,2-epoxy-3-methyl-3-phenylbutanes(89) with BF_3-etherate in Ether

% product isolated and (in brackets) the ratio of products determined from the ^{1}Hn.m.r. spectrum of the crude reaction product.

Ar	Ph	*p*-Ph-OMe	*p*-Ph-Cl	*m*-Ph-Cl
 (140)	27(10)	22(10)	16(10)	26(10)
 (189)	19(5.6)	17(3.3)	8(3.3)	-(-)
 (139)	8(2.2)	24(5.0)	6(2.5)	3(0.67)
 (207)	23(6.7)	1(0.17)	24(10)	5(1.3)
 (208)	4(1.1)	-(-)	8(3.3)	-(-)

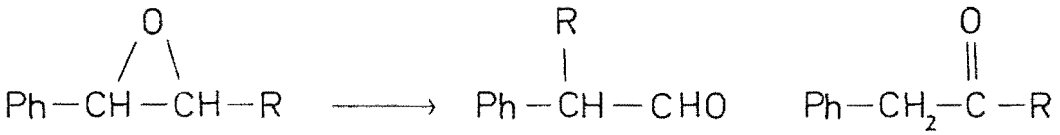
of these epoxides was carried out in benzene demonstrates that hydrogen migration after Cl-O bond cleavage does not compete with alkyl migration in this solvent. Hydrogen migration becomes competitive when the reaction is carried out in ether, and it is perhaps notable that the overall reaction of the epoxides is slower in ether(cf benzene). For the *para*-methoxy substituted epoxide(89b) there is a large increase in the amount of ketone(139b) formed.

The 2-aryl-1-ethanoxy-3-methyl-3-phenylbut-1-enes(207b, d,e) were formed in the reactions of all the substituted epoxides(89b,d,e) with BF_3-etherate in ether although only a trace amount was formed for the rearrangement of the *para*-methoxy and *meta*-chloro substituted epoxides(89b,e). The mechanism proposed for the formation of the vinyl ethers involves Cl-O bond cleavage followed by alkyl migration and nucleophilic attack by ether at the cationic center(p.137). The proposal that alkyl migration and nucleophilic attack occur almost simultaneously appears to be supported by the amount of vinyl ether formation for each of the substituted epoxides. For the phenyl and *para*-chlorophenyl epoxides(89a,d) the yield of vinyl ether is much greater than for the *para*-methoxy-phenyl and *meta*-chlorophenyl epoxides(89b,e). The rate of alkyl migration, which is governed in part by the energy of the adjacent carbocation, influences the amount of vinyl ether formed during the rearrangement. For the *para*-methoxy substituted carbocation the alkyl migration rate should be slower and for the *meta*-chloro carbocation the rate of alkyl migration faster than either phenyl or *para*-chlorophenyl intermediates. For the *meta*-chloro substituted substrate intramolecular reaction is favoured over intermolecular reaction with ether.

Di-(1R*,2S*-1-aryl-3-methyl-3-phenylbutan-2-ol)ether(208d) was isolated from the BF_3-etherate catalysed rearrangement of the *para*-chloro substituted epoxide(89d) in ether. The mechanism proposed for the formation of the dimer ether(208) requires initial formation of a diol-type intermediate by nucleophilic attack by water. The source of water in the anhydrous conditions employed in these reactions must come from the formation of vinyl ether(207) and it is notable that dimer (208) is formed only in reactions where vinyl ether is observed in significant quantities. The low yield of products isolated in some instances is attributed to decomposition of the aldehyde product on column chromotography.

(d) Reaction of *cis*-1-Aryl-1,2-epoxy-3-methyl-3-phenylbutanes with BF_3-etherate.

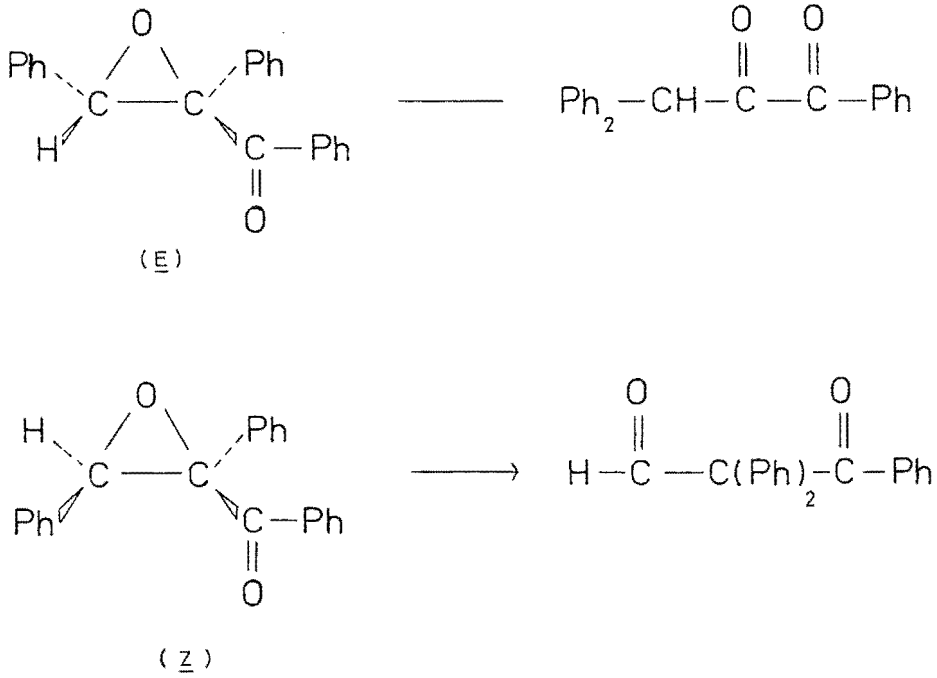
Comparisons of reactions of *cis* and *trans* epoxides with BF_3-etherate have shown that the stereochemistry of the epoxide influences the ratio of products and in some cases even determines the type of product formed. Kelly[103] found β-alkyl styrene epoxides rearranged with acid catalysts to give aldehyde and ketone products(Scheme 88) and noted



R = Me, Et, iso-Pr, t-Bu

Scheme 88

a greater proportion of the alkyl migration for the *trans*-isomers. Gorski *et al*[94] showed that treatment of S-phenyl (*E*)-2,3-diphenylthiolglycidate with BF_3-etherate in ether gave largely S-phenyl 3,3-diphenylthiolpyruvate but similar treatment of the *Z* thiolglycidate isomer gave in addition to S-phenyl 3,3-diphenylthiolpyruvate, S-phenyl 2,3-diphenyl-3-oxopropanethioate and S-phenyl 2,2-diphenyl-3-oxopropanethioate(Scheme 73). House and Rief[113] found that the BF_3-etherate catalysed rearrangement of the *E* and *Z* isomers of 2-phenylbenzalacetophenone oxide occurred by different pathways(Scheme 89).



Scheme 89

In view of the effect that stereochemistry is observed to have on the BF_3-etherate catalysed rearrangement of epoxides the *cis*-1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes(216 b,d,e) were prepared and their reactions with BF_3-etherate in benzene were studied. Short term photolyses of *trans*-1-aryl-3-methyl-3-phenylbut-1-enes(88a-g) gave rise to the *cis* alkenes(109a-g) and *trans*-1-aryl-3,3-dimethyl-2-phenylcyclopropanes(112a-g) in different ratios, depending on the

aryl substituent(Table 2). The *para*-methoxy, *para*-chloro and *meta*-chloro substituted *trans*-alkenes(88b,d,e) were photolysed for 3hr and the crude reaction mixtures were reacted with *m*-chloroperbenzoic acid to give mixtures of *cis* and *trans* epoxides(216b,d,e, 89b,d,e) and the substituted cyclopropanes(112b,d,e) which could be separated by column chromotography. The identities of the substituted cyclopropanes(112b,d,e) and *trans* epoxides(89b,d,e) were obtained by comparison of their ^{1}Hn.m.r. spectra with those of authentic samples. The stereochemistry of the *cis* epoxides(216b,d,e) was confirmed by the H1-H2 coupling constant, J = 4.5Hz, in the ^{1}Hn.m.r. spectra[63].

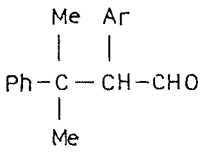
Reaction of the *cis* epoxides(216b,d,e) with BF_3-etherate in benzene gave the 2-aryl-3-methyl-3-phenylbutanals (140b,d,e) and the 1-aryl-3-methyl-3-phenylbutan-2-ones(139b,d). The ratios of these products were determined from the ^{1}Hn.m.r. spectra of the crude reaction products(Table 7) and the products were isolated by column chromotography and identified by comparison of their ^{1}Hn.m.r. and i.r. spectra with those of authentic samples. No ethanoxy alcohols(189) could be detected by ^{1}Hn.m.r. spectroscopy.

A comparison of the reactions of the *cis*- and *trans*-1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes with BF_3-etherate in benzene show that the stereochemistry of this epoxide system has a marked effect on the product ratio and the product formed. The lack of formation of ethanoxy alcohols (189) suggests that the rate of intramolecular migration for the *cis* isomers is faster than for the *trans* isomers where intermolecular reactions are competitive. The formation of the ketone products(139b,d) from the rearrangement of the *cis* epoxides(216b,d) suggests that the rate of rotation about the C1-C2 bond of the intermediate cation is more than comparable

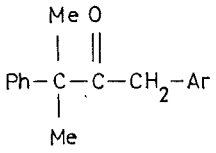
TABLE 7

Reaction of *cis*-1-Aryl-1,2-epoxy-3-methyl-3-phenylbutanes(216) with BF_3-etherate in Benzene

% product isolated and (in brackets) approximate ratio of products determined from ^{1}Hn.m.r. spectrum of crude reaction mixture.



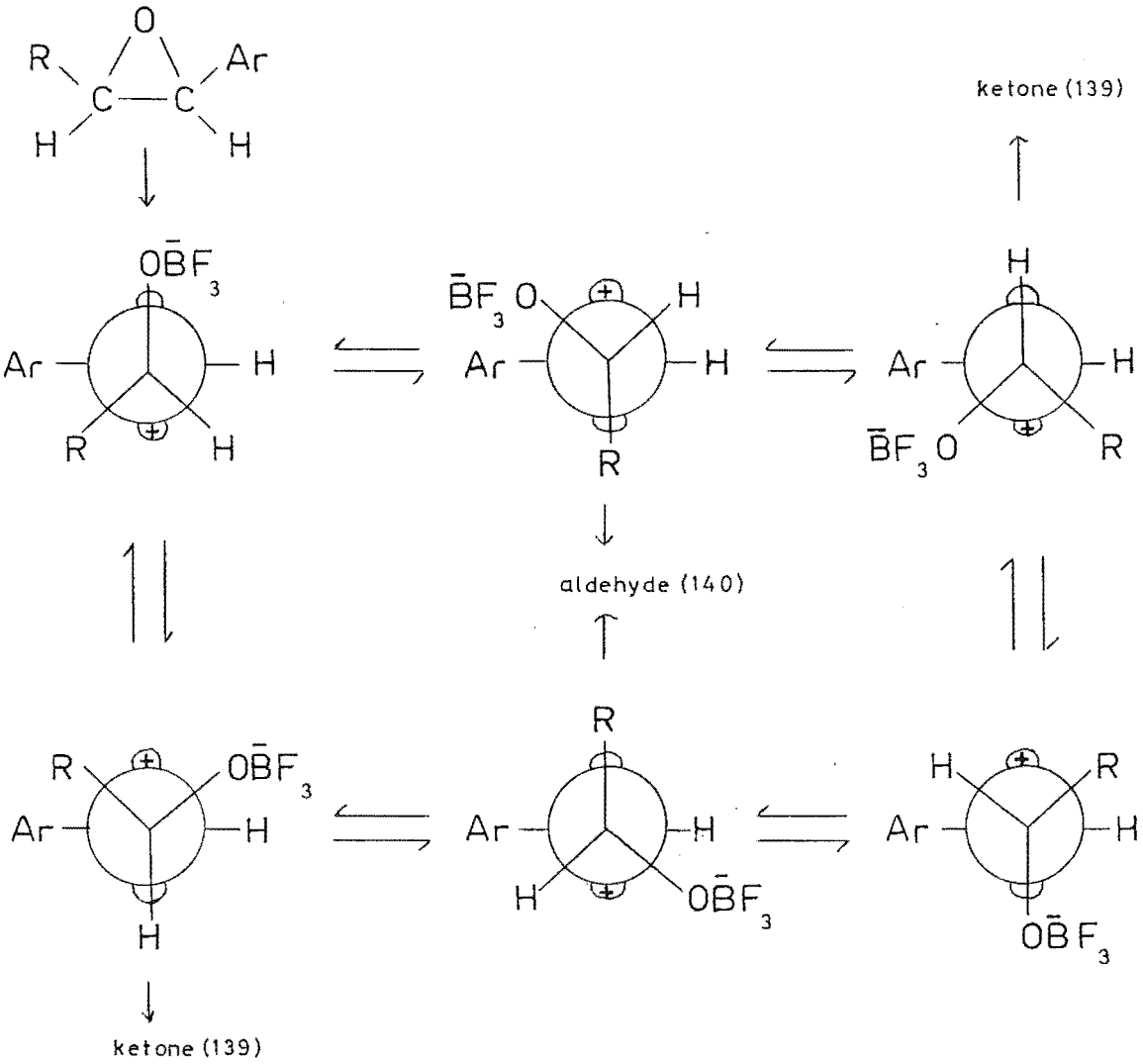
(140)



(139)

Ar	(140)	(139)
p-Ph-OMe	73 (5)	10 (1)
p-Ph-Cl	72 (20)	c.3 (1)
m-Ph-Cl	67 (1)	- (-)

with the rate of intramolecular migration(Scheme 90).



Scheme 90

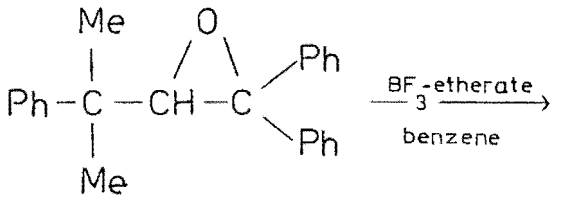
BF_3-Etherate Catalysed Rearrangements of 1,1-Diaryl-1,2-epoxy-3-methyl-3-phenylbutanes(144, 230).

The 1-aryl-1,2-epoxy-3-methyl-3-phenylbutane system(89) was found to form some unexpected products on reaction with BF_3-etherate and it was considered to be desirable to extend the investigation to the more reactive C1-diaryl substituted epoxides(I44, 230).

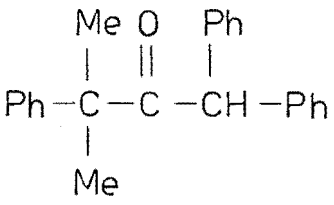
(a) Reaction of 1,1-Diphenyl-1,2-epoxy-3-methyl-3-phenylbutane(144) with BF_3-etherate.

This epoxide(144) was allowed to react with BF_3-etherate in benzene for 2min and 5min and was found to form different products for the different reaction periods.

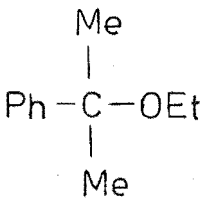
1,2-Epoxy-3-methyl-1,1,3-triphenylbutane(144) reacted with BF_3-etherate in benzene for 2min and gave 3-methyl-1,1,3-triphenylbutan-2-one(146)(6%), 2-phenylpropyl-2-(2,2-diphenylethylene)ether(217)(41%), 2-phenylpropyl-2-ethyl ether(218)(5%) and benzophenone(46).



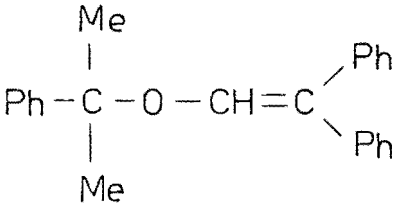
(144)



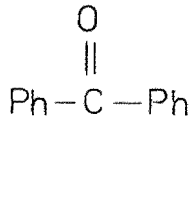
(146)(6%)



(218)(5%)

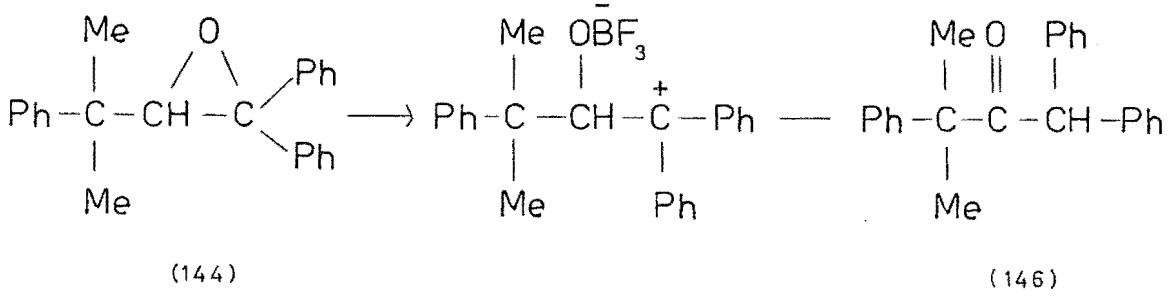


(217)(41%)



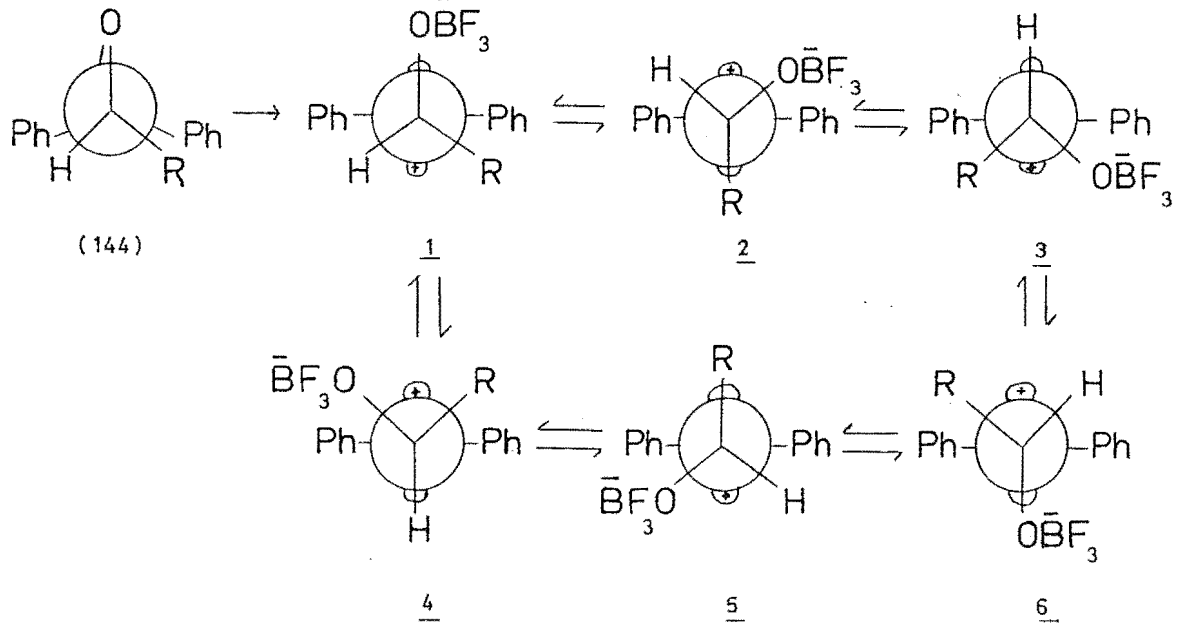
(46)(24%)

The ^{1}Hn.m.r. spectrum of 3-methyl-1,1,3-triphenyl-butan-2-one(146) showed the two methyl groups as a single peak(δ_H1.44), Hl at δ_H5.06 and a multiplet centered at δ_H7.07(Wh/2 llHz) due to the aromatic protons. The infrared spectrum showed a carbonyl absorption at ν 1715 cm^{-1} and the ^{13}Cn.m.r. spectrum displayed a single peak for the two methyl groups(δ_C24.9), a methine signal(δ_C58.7), a quaternary carbon signal(δ_C53.7), a carbonyl resonance(δ_C209.8) and eight peaks for the aromatic carbons(ClAr: 139.8, 128.4, 128.3, 126.9; C3Ar: 142.5, 126.6, 128.6, 127.1). The ketone(146) is formed by Cl-O bond cleavage followed by hydrogen migration(Scheme 91).



(144) (146)

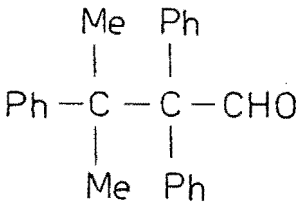
Scheme 91



(144) 1 2 3 4 5 6

Scheme 92

A study of the conformers formed on epoxide ring opening(Scheme 92) shows that rotation about the C1-C2 bond to form conformer *2* decreases the alkyl-phenyl interaction but increases the interaction between OBF_3 and the phenyl group. In this conformer the alkyl group is favourably aligned with the vacant p orbital for migration to occur. Migration of the alkyl group would result in the formation of 3-methyl-2,2,3-triphenylbutanal(219) and although aldehyde (c.5%) can be detected in the ^{1}Hn.m.r. spectrum(δ_H9.87 ,s) and i.r. spectrum(ν 2810, 2710, 1715 cm^{-1}) of the crude reaction mixture, it was not possible to isolate it by column chromotography. Alkyl migration may be disfavoured by the steric interaction between the phenyl groups on C1 and the migrating alkyl group.



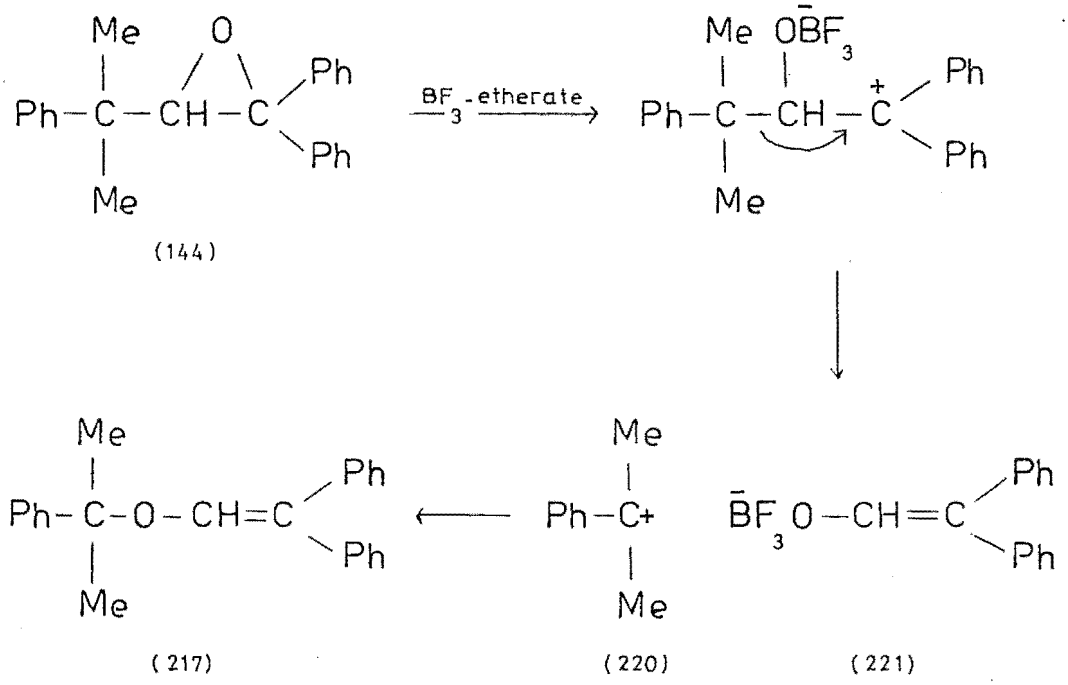
(219)

Rotation about the C1-C2 bond from conformer *2* to conformer *3* would allow hydrogen migration to occur. However, this rotation requires eclipsing of the solvated OBF_3 group and a phenyl ring. On the other hand, rotation from conformer *1* to conformer *6* also correctly aligns the hydrogen for migration but formation of this conformer requires Ph-R torsional interaction. Neither hydrogen nor alkyl migration are particularly favoured processes.

The major product, 2-phenylpropyl-2-(2,2-diphenyl-ethylene)ether(217) was identified from its ^{1}Hn.m.r. spectrum which showed the presence of two methyl groups as a single peak(δ_H1.65), a single vinyl proton signal at δ_H6.35 and a

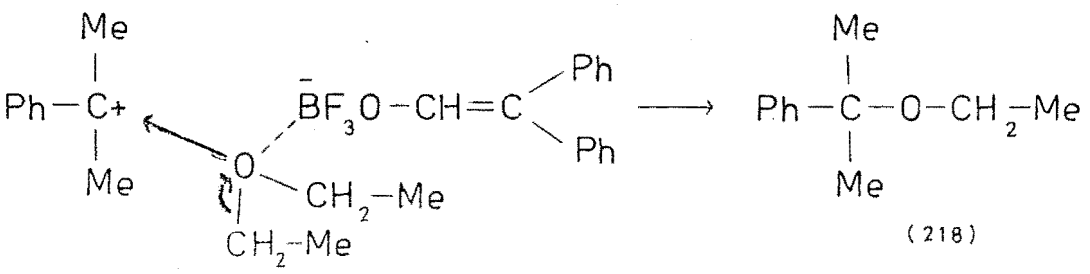
multiplet centered at δ_H7.25(Wh/2 16Hz) for the fifteen aromatic protons. The i.r. spectrum indicated the presence of a C-O-C linkage(ν 1110, 1090, 1065 cm^{-1}) and the ^{13}Cn.m.r. spectrum showed the methyl carbon signal (δ_C29.0), a quaternary carbon resonance(δ_C80.7) and ten signals due to the aromatic carbons. An sford spectrum showed that the vinyl carbon signals at δ_C140.7 and δ_C120.6 were a doublet and a singlet respectively.

The formation of the vinyl ether(217) was unexpected and is thought to be formed as shown in Scheme 93.



Scheme 93

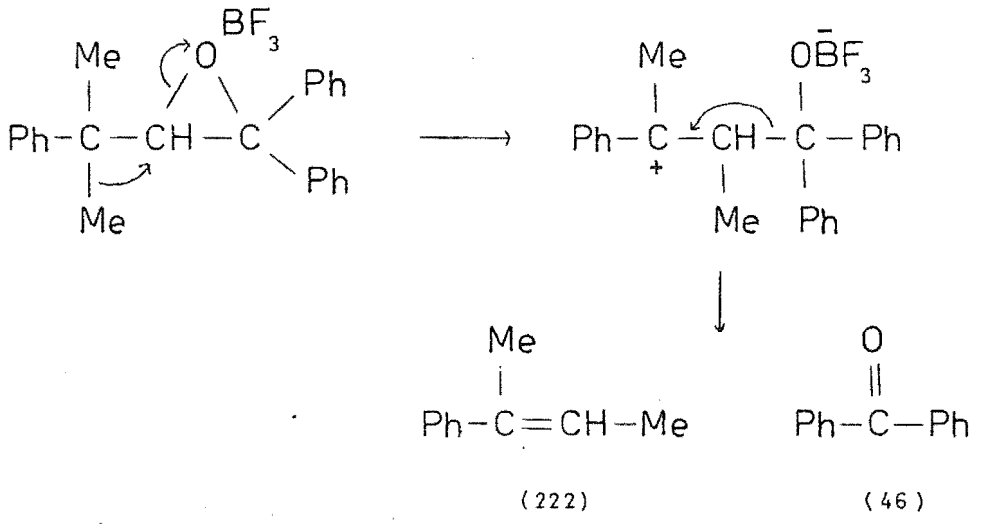
The cationic fragment(220) is also trapped by reaction with ether to give 2-phenylpropyl-2-ethyl ether(218)(Scheme 94). The ^{1}Hn.m.r. spectrum of (218) showed two



Scheme 94

methyl groups as a single peak(δ_H1.52) and the ethoxy group as a triplet(δ_H1.12, J 7Hz, Me) and an AB quartet(δ_H3.07, 3.30, J 7Hz, CH_2). A multiplet centered at δ_H7.25(Wh/2 10Hz) showed the presence of the five aromatic protons. The ^{13}Cn.m.r. spectrum also showed the methylene and methyl carbon signals(δ_C58.0, 15.8) of the ethoxy group, the methyl carbons peak (δ_C28.5) and four peaks due to the phenyl ring(δ_C145.5, 127.7, 128.4, 125.6).

The formation of benzophenone(46) was surprising since C2-O bond cleavage was not expected to compete with C1-O bond cleavage. For the previous study of 1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes(89), no C2-O bond cleavage was observed. The mechanism proposed for the formation of benzophenone(46) involves methyl migration from C3 to C2 which induces C2-O bond cleavage(Scheme 95).

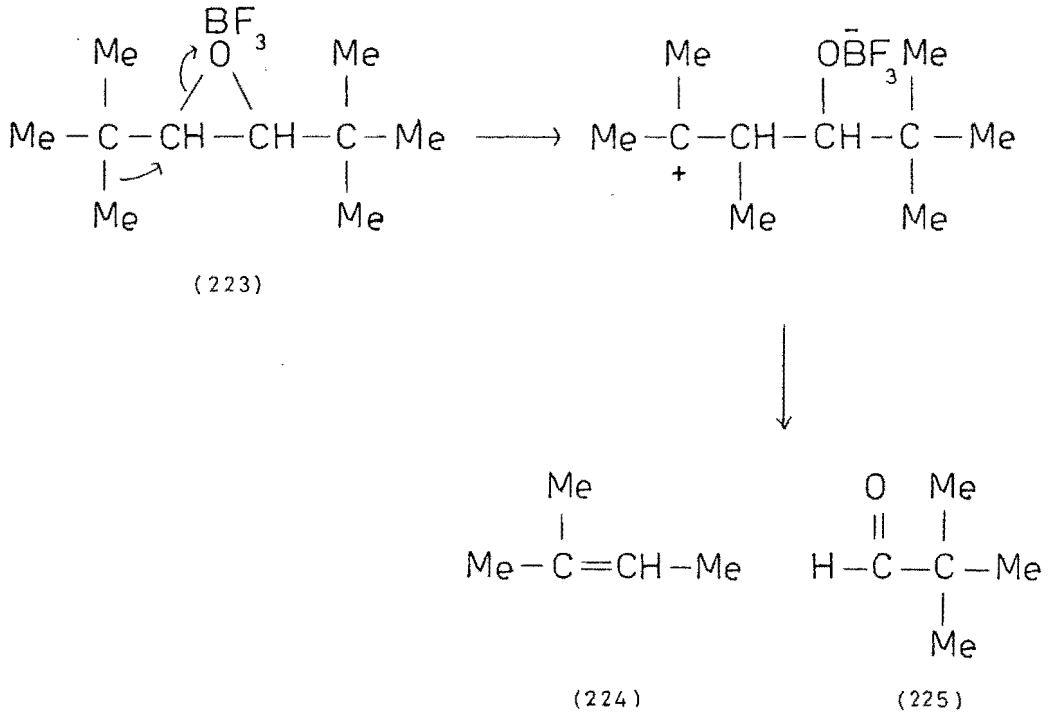


(222) (46)

Scheme 95

Fragmentation results in the formation of benzophenone(46) and 2-phenylbut-2-ene(222)[114] however the alkene(222) was not detected in the reaction mixture. The proposed mechanism is analogous to that suggested for the BF_3-etherate catalysed rearrangement of 3,4-epoxy-2,2,5,5-tetramethyl-hexane(223) to 2-methylbut-2-ene(224) and pivalaldehyde(225)

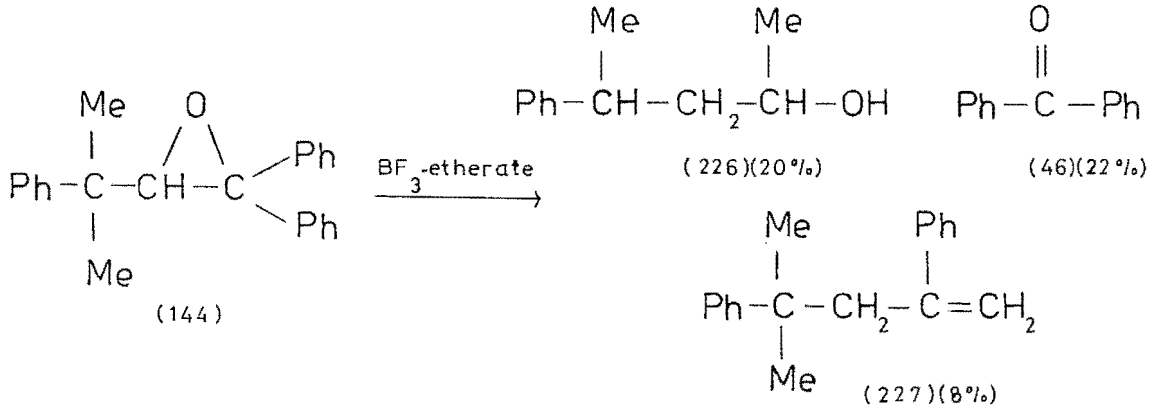
(Scheme 96)[97].



(223) (224) (225)

Scheme 96

In contrast to the above results, reaction of 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144) with BF_3-etherate in benzene for 5min gave 4-phenylpentan-2-ol(226) (20%), 2,4-diphenyl-4-methylpent-1-ene(227)(8%) and

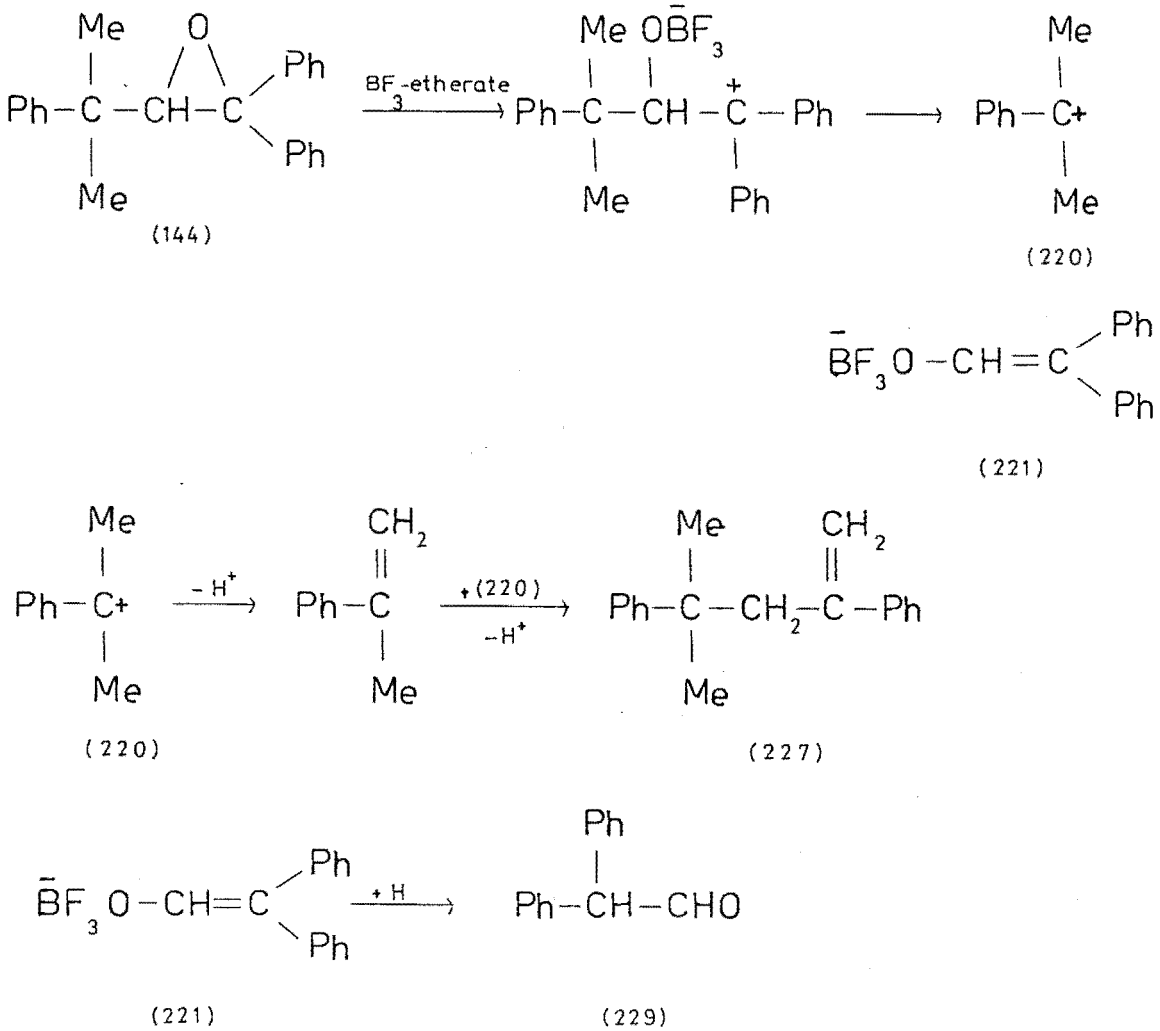


(144) (226)(20%) (46)(22%) (227)(8%)

benzophenone(46)(22%). The ^{1}Hn.m.r. spectrum of 4-methyl-2, 4-diphenylpent-1-ene(227) showed the two methyl groups as a single peak(δ_H1.20), the methylene signal at δ_H2.80, the terminal vinyl proton resonances at δ_H4.72 and δ_H5.08 and a multiplet centered at δ_H7.12(Wh/2 3Hz) represented ten aromatic protons. The ^{13}Cn.m.r. spectrum showed the methyl

peak (δ_C28.7), the methylene carbon signal(δ_C49.6), a quaternary carbon peak(δ_C38.6), two vinyl carbon signals (δ_C116.8, 149.4) and eight peaks for the two phenyl rings.

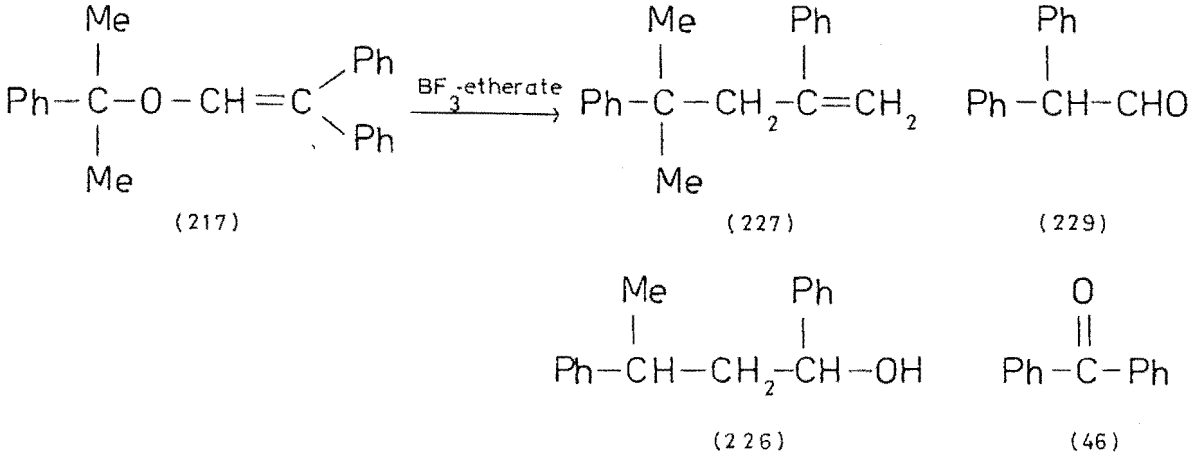
The mechanism proposed for the formation of this alkene(227) is shown in Scheme 97. C1-O bond cleavage is followed by C2-C3 bond cleavage resulting in the formation of the cation(220) and the anion(221). The cation(220) loses hydrogen to form the alkene(228) which undergoes reaction with the cation(220) to form the alkene(227). The alkene(221) can gain hydrogen to form the aldehyde(229). In this reaction the ^{1}Hn.m.r. spectrum of the crude reaction product shows the presence of an aldehyde(c. 15%)(δ_H9.80, J 2.5Hz, 4.69, J 2.5Hz) which could not be isolated by column chromotography.



Scheme 97

The ^{1}Hn.m.r. spectrum of 4-phenylpentan-2-ol(226) showed two methyl groups as doublets(δ_H1.15, 1.25, J 5Hz) and a hydroxyl signal at δ_H1.40. Methylene protons appeared as a complex multiplet centered at δ_H1.80(Wh/2 20Hz) and two methine protons appeared as multiplets centered at δ_H2.82 and δ_H3.67. A single peak at δ_H7.03 showed the presence of five aromatic protons. The ^{13}Cn.m.r. spectrum showed the presence of two methyl signals(δ_C22.3, 23.6), a methylene carbon peak(δ_C47.8), two methine carbon signals (δ_C36.8, 66.2) and four aromatic peaks(δ_C147.2, 126.8, 128.5, 126.0). The mechanism of the formation of this alcohol(226) remains unexplained.

In order to determine if the products(226, 227) formed in the longer term reaction(5min) were the secondary products formed by the action of BF_3-etherate on those products(146, 217) isolated from the short term reaction(2min), 2-phenylpropyl-2-(2,2-diphenylethylene)ether(217) was reacted with BF_3-etherate in benzene for 5min. 4-Phenylpentan-2-ol(226), 4-methyl-2,4-diphenylpent-1-ene(227), an aldehyde(229) and benzophenone(46) could be detected in the reaction mixture by ^{1}Hn.m.r. and infrared spectroscopy. These products when formed in the long term reaction(5min) can therefore be assumed to be formed as secondary products in the reaction

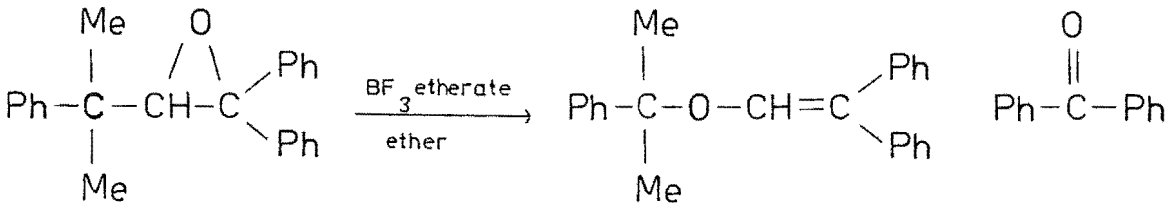


(217) (227) (229)

(226) (46)

of the epoxide(144) with BF_3-etherate. 3-Methyl-1,1,3-triphenylbutan-2-one(146) reacted very slowly with BF_3-etherate and only a small amount(c.7%) of benzophenone(46) was separated from the unreacted ketone(146) after 0.5hr. The rate of this reaction excludes the intermediacy of the ketone(146) in the formation of benzophenone(46) from the epoxide(144) on reaction with BF_3-etherate.

As previously described, a change in reaction medium from benzene to ether can affect a change in the products formed on reaction of an epoxide with BF_3-etherate. Accordingly,the reaction of 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144) with BF_3-etherate was carried out in ether. This reaction was slower than the reaction in benzene and after 0.5hr the primary products 2-phenylpropyl-2-(2,2-diphenylethylene)ether(2.7)(47%) and benzophenone(46)(23%) were isolated.

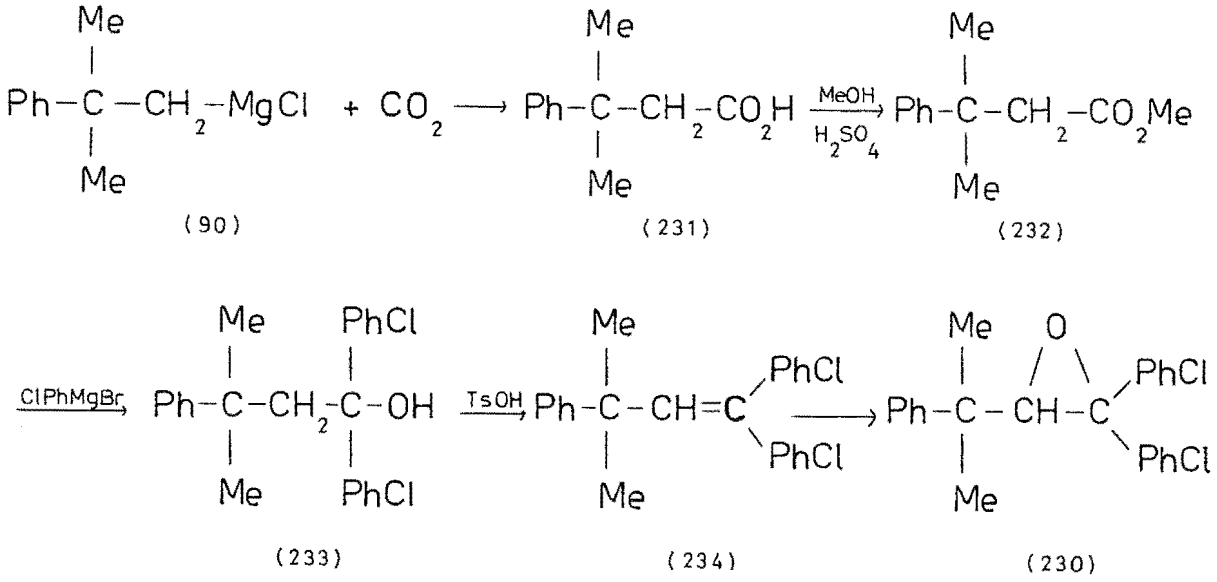


(144) (217) (46)

(b) Reaction of 1,1-Bis-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(230) with BF_3-etherate.

In view of this rather unusual series of products formed in the BF_3-etherate catalysed rearrangement of the epoxide(144), the chloro-substituted epoxide, 1,1-bis-(4'-chlorophenyl)-1, 2-epoxy-3-methyl-3-phenylbutane(230) was prepared and its reaction with BF_3-etherate studied.

2-Methyl-2-phenylpropylmagnesium chloride(90) was reacted with carbon dioxide to give 3-methyl-3-phenylbutanoic acid(231)[115]. Esterification with methanol and sulphuric acid gave methyl-3-methyl-3-phenylbutanoate(232)[58] which on reaction with *para*-chloro-phenylmagnesium bromide gave 1,1-bis-(4'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(233) (Scheme 98). The ^{1}Hn.m.r. spectrum of the alcohol(233)



Scheme 98

showed the two methyl groups as a single peak(δ_H1.07), the hydroxyl proton signal(δ_H1.77), the methylene proton resonance(δ_H2.75) and a narrow multiplet centered at δ_H7.10 (Wh/2 3Hz) for the aromatic protons. The ^{13}Cn.m.r. spectrum showed the methyl carbon signals(δ_C30.8) and the C2 carbon peak(δ_C53.7). The quaternary carbon C3 peak appeared at

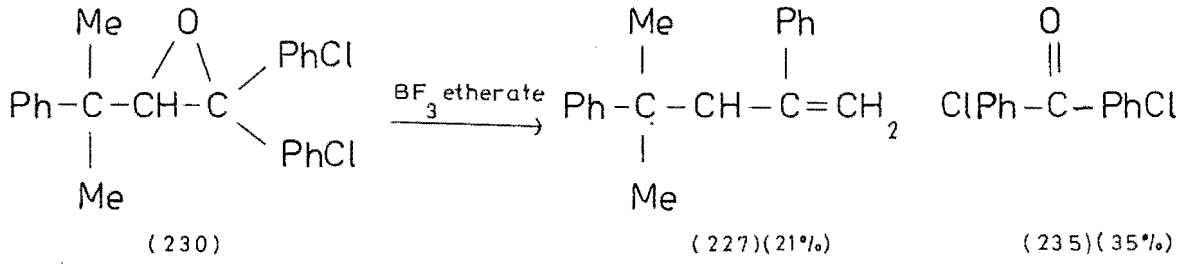
δ_C37.8 and the Cl signal at δ_C77.3. Eight peaks represented the three aromatic rings(ClAr:δ_C146.5, 125.8, 128.0, 132.3; C3Ar:δ_C148.4, 126.9, 128.5, 126.1).

Reaction of (233) with *p*-toluenesulphonic acid gave 1,1-bis-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(234). The ^{1}Hn.m.r. spectrum of the alkene(234) showed the two methyl groups as a single peak(δ_H1.28), a single vinyl proton peak(δ_H6.35) and a multiplet centered at δ_H6.95(Wh/2 6Hz) represented the aromatic protons. The ^{13}Cn.m.r. spectrum showed the methyl carbon signal(δ_C30.9) and the quaternary C3 peak(δ_C40.6). The vinyl carbon signals appeared at δ_C140.5(C1) and δ_C137.8(C2) and eleven peaks represented the three aromatic rings(ClAr: δ_C141.6, 138.5, 131.2, 128.1, 127.7, 132.8, 132.7; C3Ar: δ_C149.9, 125.9, 127.9, 125.5).

Reaction of the alkene(234) with *m*-chloroperbenzoic acid gave 1,1-bis-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(230). The ^{1}Hn.m.r. spectrum of the epoxide(230) showed two peaks for the methyl protons(δ_H1.05, 1.18). The C2 proton resonance appeared at δ_H3.42 and a multiplet centered at δ_H7.12(Wh/2 8Hz) represented the aromatic protons. The ^{13}Cn.m.r. spectrum showed two methyl signals (δ_C24.1, 28.2) and the quaternary C3 peak(δ_C38.9). The C1 signal appeared at δ_C65.2 and C3 at δ_C74.2. The three aromatic rings were represented by twelve peaks.

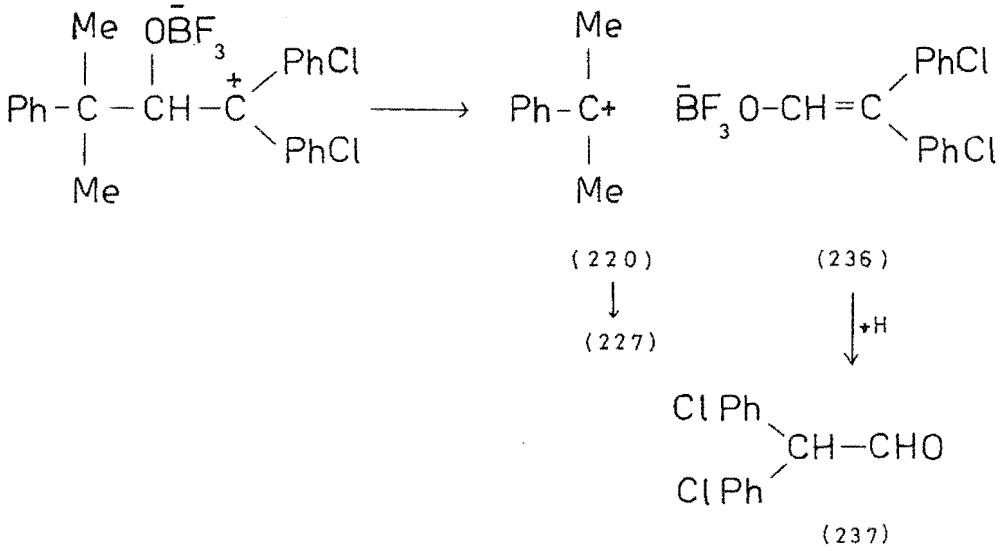
The reaction of the epoxide(230) with BF_3-etherate was again effected for different times(5min, 2min, 0.5min) to determine the effect of the chloro substituent on the formation of the primary and secondary products. Reactions over 5min and 2min gave the same products and reaction for the shorter period of 0.5min was required to isolate a primary reaction product.

Reaction of 1,1-bis-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(230) with BF_3-etherate in benzene for 5min and 2min gave 2,4-diphenyl-4-methylpent-1-ene(227)(21% and 22% respectively) and bis-(4'-chlorophenyl)ketone(35% and 30% respectively). An aldehyde product(c. 20%) was also



(230) (227)(21%) (235)(35%)

detected in the ^{1}Hn.m.r.(δ_H9.83, J 2Hz, 4.80, Wh/2 5Hz) and i.r.(ν 1725, 2720, 2820 cm^{-1}) spectra of the crude reaction product but it was not possible to isolate this compound by column chromotography. 2,4-Diphenyl-4-methylpent-1-ene(227) was identified by comparison with an authetic sample formed by the BF_3-etherate reaction of epoxide(144)(p.161). The reaction mechanism proposed for the formation of the alkene (227) is outlined in Scheme 97. The alkene(236) formed on C2-C3 bond cleavage can rearrange to form an aldehyde(237) and the



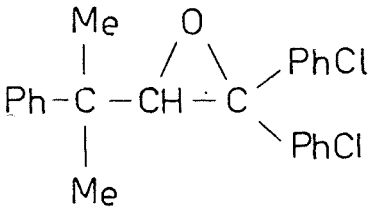
Scheme 99

^{1}Hn.m.r. spectrum of the crude reaction product(δ_H9.83, J 2Hz) is consistent with the presence of this aldehyde(237) in the reaction mixture.

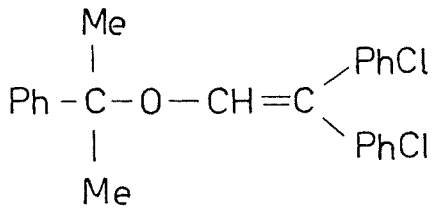
The mechanism of formation of bis-(4'-chlorophenyl) ketone(235) is analogous to the formation of benzophenone(46) in the reaction of the phenyl substituted epoxide(144) with BF_3-etherate(Scheme 94). No signals due to 2-phenylbut-2-ene(222) were detected in the ^{1}Hn.m.r. spectrum of the reaction product. The alcohol(226) formed in the longer term(5min) reaction of the phenyl substituted epoxide(144) was not detected in the rearrangement of the chlorophenyl substituted epoxide(230).

The epoxide(230) was reacted with BF_3-etherate in benzene for 0.5min to give 2-phenylpropyl-2-(2,2-bis-(4'-chlorophenyl)ethylene)ether(238)(25%), bis-(4'-chlorophenyl) ketone(235)(28%) and 2,4-diphenyl-4-methylpent-1-ene(227)(2%). The aldehyde(237)(c.20%) was detected in the ^{1}Hn.m.r. and i.r. spectra of the reaction mixture but could not be isolated by chromotography.

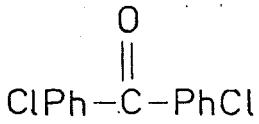
The ^{1}Hn.m.r. spectrum of the ether(238) showed the two methyl groups as a single peak(δ_H1.65), the single vinyl proton signal at δ_H6.25 and a multiplet centered at δ_H7.07 represented the aromatic protons. The ^{13}Cn.m.r. spectrum showed the methyl carbon signal(δ_C29.0) and the quaternary carbon peak(δ_C81.2). The two vinyl carbon signals appeared at δ_C118.5 and δ_C141.4 and the three aromatic rings were represented by ten peaks. The mechanism for the formation of this compound(238) is analogous to that outlined for the phenyl analogue(Scheme 92).



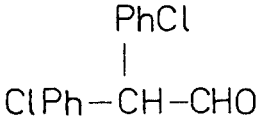
(230)



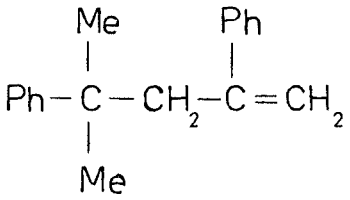
(238)(25%)



(235)(28%)



(237)(c.20)



(227)(2%)

CONCLUSION

The reactions of the aryl substituted epoxides with BF_3-etherate reported in this thesis have shown marked sensitivity to both substituent and solvent changes. The *trans*-1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes(89) reacted with BF_3-etherate in benzene to give the 2-aryl-3-methyl-3-phenylbutanals(140), by C1-O bond cleavage and alkyl migration and the 1R*,2R*-1-aryl-1-ethanoxy-3-methyl-3-phenylbutan-2-ols (189), by nucleophilic attack at the C1 cationic center. The amount of intermolecular attack is seen to increase with the stability of the intermediate carbocation formed on epoxide ring opening(p.145). Reaction of these epoxides(89) with BF_3-etherate in ether gives rise to ketone(139), vinyl ether(207) and dimeric ether(208) products, in addition to the aldehydes(140) and ethanoxy alcohols(189). The slower reaction rate in ether enables hydrogen migration, which forms the ketones(139), to compete with alkyl migration which results in aldehyde(140) formation. The proportions of products formed in these reactions depend on the C1-aryl substituent(Table 5) and also on the batch of BF_3-etherate used. Vinyl ether(207) formation was not observed when a new bottle of BF_3-etherate was used for these reactions.

The *cis*-1-aryl-1,2-epoxy-3-methyl-3-phenylbutanes(216) react more rapidly with BF_3-etherate in benzene than the *trans*-epoxides and intermolecular attack does not compete with intramolecular group migration.

Replacement of the C1-hydrogen of the epoxide(89) by a second phenyl group completely alters the reaction pathway on rearrangement catalysed by BF_3-etherate. Intramolecular group migration products are detected only in trace amounts and intermolecular nucleophilic attack is not

observed. One of the major reaction processes involves C1-O bond cleavage followed by fragmentation(C2-C3). Recombination of the fragments form an ether(217) which can react further with BF_3-etherate to give secondary reaction products(226, 227). The other reaction observed is the formation of benzophenone(46). The proposed mechanism involves C2-O bond cleavage and fragmentation of the resulting carbocation.

The BF_3-etherate catalysed rearrangements of epoxide systems have been extensively studied and found to undergo a wide range of reactions depending on the structure of the epoxide. In this study typical aryl substituent effects were observed, *cis*- and *trans*-epoxides formed different products, diaryl substitution completely changed the reaction pathway and a change in solvent had a marked effect on the products formed. The reagent BF_3-etherate was itself found to affect the products formed in a reaction. The sensitivity of the reaction of epoxides to the batch of BF_3-etherate being used, even when the reagent is distilled several times, points the need to caution in interpreting the mechanism of such reactions.

EXPERIMENTAL

Infrared spectra were recorded on a Shimadzu IR27G spectrometer, ultraviolet spectra on a Varian Super Scan 3 spectrometer for cyclohexane solutions and mass spectra on an A.E.I. MS902 spectrometer. Elemental analyses were determined at the University of Otago. ^{1}H n.m.r. spectra were recorded on Varian T60 or EM360A spectrometers for $CDCl_3$ or CCl_4 solutions with Me_4Si as an internal standard. ^{13}C n.m.r. spectra were recorded on a Varian CFT20 spectrometer for $CDCl_3$ solutions with Me_4Si as an internal standard.

The alumina for chromotography was Spence Grade H, used directly or deactivated by the addition of 10% V/V of water. Silver nitrate alumina was prepared by the addition of 100g alumina to a solution of 10g $AgNO_3$ in 20ml water and 50ml methanol and evaporation of the mixture to dryness under reduced pressure. The silver nitrate alumina was reactivated by heating at 120^{o}C overnight. For dry column chromotography I.C.N. Pharmaceuticals alumina Brockman activity III/20 was used.

A Varian aerograph 1400 with SE 30(2½%) on Chromosorb W column was used for all analytical g.l.c. Photolysis was carried out in a Rayonet photochemical reactor manufactured by Southern New England Ultra Violet Company. All solvents and reagents used in the following experiments were purified using standard methods and distilled before use.

Grignard reaction of 2-methyl-2-phenylprop-1-yl magnesium chloride(90) with benzaldehyde.

(i) A solution of 2-methyl-2-phenylprop-1-yl chloride (3.9g) in dry tetrahydrofuran was added slowly to a warm mixture of magnesium(0.9g) in dry tetrahydrofuran and heated under reflux for 3hr. After cooling to room temperature redistilled benzaldehyde(3.2g) in dry tetrahydrofuran was slowly added and the resulting mixture heated under reflux for 1hr, cooled to room temperature and stirred for 2hr. Saturated ammonium chloride solution was added and the product isolated by means of ether. After removal of solvent the crude reaction product deposited crystals(1.77g) m.p.134-136^{o}C. Recrystallisation from chloroform afforded two distinct crystalline forms which were manually separated to give dl-2,7-dimethyl-2,4,5,7-tetraphenyloctane-4,5-diol (91a) as long needles, m.p. 152-154^{o}C(Found: M^{+},239.1420; C, 85.4; H, 7.9. $C_{34}H_{38}O_2$ requires M^{+}, 478.2872; C, 85.3; H, 8.0%. ½($C_{34}H_{38}O_2$) requires M^{+}, 239.1435). $\nu_{max}(CHCl_3)$ 3590cm^{-1}. ^{1}H n.m.r. δ 0.75, C2Me, C7Me; 1.00, C1H_3, C8H_3; 1.68, J 15Hz, H3, H6; 2.02, OH; 2.75, J 15Hz, H3', H6'; 7.20, Wh/2 4Hz, ArH's. ^{13}C n.m.r. δ 27.4$_8$, C1, C8; 34.4$_4$, C2Me, C7Me; 37.5$_4$, C2, C7; 45.7$_4$, C3, C6; 81.4$_1$, C4, C5; 150.0$_4$, C2-, C7ipso C's; 142.2$_2$, C4-, C5ipso C's; 125.7$_7$, C2-, C4-, C5-, C7ortho C's; 128.4$_1$, C2-, C4-, C5-, C7meta C's; 126.5$_3$, C2-, C4-, C5-, C7para C's and meso-2,7-dimethyl-2,4,5,7-tetraphenyloctane-4,5-diol(91b) as irregular hexagonal plates, m.p.178-179^{o}C(Found: M^{+}, 239.1441; C, 85.4; H, 7.9. $C_{34}H_{38}O_2$ requires M^{+}, 478.2872; C, 85.3; H, 8.0%. ½($C_{34}H_{38}O_2$) requires M^{+}, 239.1435). $\nu_{max}(CHCl_3)$ 3600cm^{-1}. ^{1}H n.m.r. δ 0.75, C2Me, C7Me; 0.90, C1H_3, C8H_3; 1.39, OH; 2.22, C3H_2, C6H_2; 6.95, Wh/2 50Hz, ArH's. ^{13}C n.m.r. δ26.6$_5$, C1, C8; 35.1$_3$, C2Me, C7Me; 37.1$_5$, C2, C7; 46.9$_3$, C3, C6;

81.5_0, C4, C5; 149.1_4, C2-, C7ipso C's; 126.2_6, C2-, C7-ortho C's; 128.3_3, C2-, C7meta C's; 125.5_8, C2-, C7para C's; 144.6_2, C4-, C5ipso C's; 125.3_9, C4-, C5ortho C's; 128.3_3, C4-, C5meta C's; 127.9_0, C4-, C5para C's.

The mother liquors were concentrated and the residue remaining was absorbed onto alumina(200g). Elution with light petroleum gave 2-methyl-2-phenylpropane(94)(0.7g) ^{1}H n.m.r. δ 1.30, Me; 7.25, Wh/2 10Hz, ArH's. Further elution with light petroleum-ether(50:1) afforded 1,3-phenyl-3-methylbutan-1-one(92a)(0.8g)(Found: M^+, 238.1366; C, 85.6; H, 7.4. $C_{17}H_{18}O$ requires M^+, 238.1357; C, 85.7; H, 7.6%). ν_{max}(neat) 1690, 1670cm^{-1}. λ_{max} 211nm(ε6058), 238(7885), 278.5(769), 287.5(577). ^{1}H n.m.r. δ 1.50, C3Me, $C4H_3$; 3.27, $C2H_2$; 7.50, Wh/2 43Hz, ArH's. ^{13}C n.m.r. δ 199.0_4, C1; 50.8_8, C2; 37.5_2, C3; 29.1_1, C3Me, C4; 138.2_1, C1ipso C; 128.3_8, 128.0_7, C1ortho C, C1meta C; 132.6_5, C1para C; 148.8_8, C3ipso C; 125.4_6, C3ortho C; 128.1_7, C3meta C; 125.7_8, C3para C. Elution with ether gave benzyl alcohol(93) (2.5g) ^{1}H n.m.r. δ 3.38, Wh/2 6Hz, OH; 4.45, CH_2; 7.12, ArH's.

(ii) A solution of 2-methyl-2-phenylprop-1-yl chloride (3.2g) in dry tetrahydrofuran was added to a heated mixture of magnesium(0.9g) in dry tetrahydrofuran and the resulting mixture was heated under reflux for 3hr. The Grignard reagent was stirred and cooled to 0°C in a nitrogen atmosphere and redistilled benzaldehyde(3.2g) in tetrahydrofuran slowly added. The resulting mixture was allowed to stand at room temperature for 12hr. Saturated ammonium chloride solution was added and the product isolated by means of ether. After the removal of solvent the oily residue was absorbed onto an alumina dry column(270g) and light petroleum-

ether(4:1) percolated through the column. Elution of the segment c. Rf 1 to 0.87 with ether gave 2-methyl-2-phenyl-propane(94)(0.07g) ^{1}H n.m.r. δ 1.30, Me; 7.25, ArH's. Elution of the segment c. Rf 0.87 to 0.60 with ether gave 1,3-diphenyl-3-methylbutan-1-one(92a)(2.68g) ^{1}H n.m.r. δ 1.50, C3Me, $C4H_3$; 3.27, $C2H_2$; 7.50, Wh/2 43Hz, ArH's. Elution of the segment c. Rf 0.60 to 0.47 with ether gave 1,3-diphenyl-3-methylbutan-1-ol(97a)(0.22g, m.p. 89-91°C) (Found: M^+, 240.1479. $C_{17}H_{20}O$ requires M^+, 240.1513). ν_{max}(nujol) 3450cm^{-1}. ^{1}H n.m.r. δ 1.38, C3Me; 1.42, $C4H_3$; 1.55, OH; 2.08, Wh/2 11Hz, $C2H_2$; 4.40, J 5Hz, J 7Hz, H1; 7.26, Wh/2 2 Hz, ArH's. ^{13}C n.m.r. δ 72.3_4, C1; 53.9_7, C2; 37.5_6, C3; 29.2_5, C3Me; 29.8_9, C4; 145.9_0, C1ipso C; 125.6_1, C1ortho C; 128.3_7, C1meta C; 127.2_1, C1para C; 148.7_1, C3ipso C; 126.0_1, C3ortho C; 128.3_7, C3meta C; 125.9_1, C3para C. Elution of segment c. Rf 0.47 to 0.07 gave benzyl alcohol(93)(1.93g) ^{1}H n.m.r. δ 3.38, Wh/2 6Hz, OH; 4.45, CH_2; 7.12, ArH's.

(iii) A solution of 2-methyl-2-phenylprop-1-yl chloride(10g) in dry tetrahydrofuran(150ml) was added to a warm suspension of magnesium(2g) in dry tetrahydrofuran and the resulting mixture was heated under reflux for 3hr. The solution was decanted from the excess magnesium under a nitrogen atmosphere and cooled in an ice bath. A solution of redistilled benzaldehyde(10g) in dry tetrahydrofuran (150ml) was slowly added to the stirred solution and the resulting mixture was allowed to come to room temperature. After 1hr saturated ammonium chloride solution was added and the product isolated by means of ether. After the removal of solvent the residue was crystallised from methanol to give 1,3-diphenyl-3-methylbutan-1-ol(97a)(13g) ^{1}H n.m.r. δ 1.38, C3Me; 1.42, $C4H_3$; 1.55, OH; 2.08, Wh/2

11Hz, $C2H_2$; 4.40, J 5Hz, J 7Hz, H1; 7.26, Wh/2 2Hz, ArH's.

2,7-Dimethyl-2,5,5,7-tetraphenyloctan-4-one(95)

p-Toluenesulphonic acid(0.4g) was added to a solution of meso- and dl-2,7-dimethyl-2,4,5,7-tetraphenyloctane-4,5-diol(91a,b)(1.5g) in benzene and the resulting mixture was heated under reflux for 8hr in a Dean and Stark appartus. The reaction mixture was cooled and washed with water, saturated sodium bicarbonate solution, water and saturated sodium chloride solution, and dried. The solvent was removed to give 2,7-dimethyl-2,5,5,7-tetraphenyloctan-4-one(95) (1.45g) as a pale yellow oil(Found: M^+, 299.1726 and 161.0955; C, 88.6; H, 8.3. $C_{34}H_{36}O$ requires M^+, 460.2764; C, 88.6; H, 7.9%; $M^+-C_{11}H_{13}O$ requires 299.1799; $M^+-C_{23}H_{23}$ requires 161.0966). ν_{max}(neat) 1715cm^{-1}. ^1H n.m.r. δ 1.00, C7Me, $C8H_3$; 1.30, $C1H_3$, C2Me; 2.70, $C6H_2$; 2.92, $C3H_2$; 7.15, Wh/2 22Hz, ArH's. ^{13}C n.m.r. δ 29.8_9, C1, C2Me; 37.9_7, C2; 50.5_0, C3; 202.9_5, C4; 65.8_1, C5; 49.6_2, C6; 36.9_9, C7; 28.5_5, C7Me, C8; 149.2_7, 150.3_7, C2-, C7ipso C's; 141.2_1, C5ipso C's; 130.2_8, C5ortho C's; 127.7_3, C5meta C's; 127.8_9, 127.6_7, C2-, C7meta C's; 126.6_9, 125.4_8, 125.2_6, 124.7_9, C2-, C7ortho C's, C2-, C5-, C7para C's.

Reaction of meso- and dl-2,7-dimethyl-2,4,5,7-tetraphenyloctane-4,5-diol(91a,b) with periodic acid[116].

An etheral solution of periodic acid(2.5ml, 0.7M) was added to a solution of meso- and dl-2,7-dimethyl-2,4,5,7-tetraphenyloctane-4,5-diols(91a,b)(0.03g, c.1:1) in ether and the resulting mixture kept at room temperature for 18hr. The ether layer was decanted from the precipitate. The colourless oil isolated on the removal of the solvent was 1,3-diphenyl-3-methylbutan-1-one(92a)(0.03g) ^1H n.m.r.

δ 1.50, C3Me, $C4H_3$; 3.27, $C2H_2$; 7.50, Wh/2 43Hz, ArH's.

Reaction of 1,3-diphenyl-3-methylbutan-1-ol(97a) with methylmagnesium iodide and benzaldehyde.

Methylmagnesium iodide was prepared by the addition of iodomethane(0.6g) in dry tetrahydrofuran(20ml) to a mixture of magnesium(0.1g) in dry tetrahydrofuran(10ml). After the reaction was complete the mixture was allowed to stand at room temperature and the clear solution decanted under nitrogen. To this solution 1,3-diphenyl-3-methylbutan-1-ol(97a)(1.0g) in dry tetrahydrofuran(25ml) was rapidly added and the mixture heated under reflux for 30min. The mixture was cooled to room temperature and a solution of benzaldehyde(0.4g) in dry tetrahydrofuran(20ml) added. The resulting mixture was heated under reflux for 30min. Saturated ammonium chloride was added and the product extracted with ether. After the removal of solvent the residue was absorbed onto alumina(80g). Elution with light petroleum-ether(50:1) gave 1,3-diphenyl-3-methylbutan-1-one(92a)(0.10g) ^1H n.m.r. δ 1.50, C3Me, $C4H_3$; 3.27, $C2H_2$; 7.50, Wh/2 43Hz, ArH's and benzaldehyde(0.14g) ^1H n.m.r. δ 7.75, Wh/2 36Hz, ArH's; 9.95, CHO. Further elution with light petroleum-ether(5:1) gave 1,3-diphenyl-3-methylbutan-1-ol(97a)(0.74g) ^1H n.m.r. δ 1.38, C3Me; 1.42, $C4H_3$; 1.55, OH; 2.08, Wh/2 11Hz, $C2H_2$; 4.40, J 5Hz, J 7Hz, H1; 7.26, Wh/2 2Hz, ArH's and benzyl alcohol(93)(0.04g) ^1H n.m.r. δ 3.38, OH; 4.45, CH_2; 7.12, ArH's.

Reaction of 1,3-diphenyl-3-methylbutan-1-one(92a) with magnesium-magnesium iodide.

Iodine(0.5g) was added to a stirred suspension of magnesium(0.2g) in dry tetrahydrofuran and the resulting

mixture heated under reflux until the solution was colourless. A solution of 1,3-diphenyl-3-methylbutan-1-one(92a) (0.5g) in dry tetrahydrofuran was added to the warm mixture of magnesium iodide and the resulting mixture was heated under reflux for 4hr.After cooling the reaction mixture was decanted from excess magnesium which was washed with ether. The product was extracted with ether, washed with dilute sulphuric acid, sodium bisulphite and water and dried over anhydrous sodium sulphate. After the removal of solvent the residue was shown by ^{1}H n.m.r. spectroscopy to contain meso- and dl-2,7-dimethyl-2,4,5,7-tetraphenyloctane-4,5-diols(91a,b)(c. 50%) dl : ^{1}H n.m.r. δ 0.75, C2Me, C7Me; 1.00, $C1H_3$, $C8H_3$; 1.68, J 15Hz, H3, H6; 2.02, OH; 2.17, J 15Hz, H3', H6'; 7.20, ArH's; meso: ^{1}H n.m.r. δ 0.75, C2Me, C7Me; 0.90, $C1H_3$, $C8H_3$; 1.39, OH; 2.22, $C3H_2$, $C6H_2$; 6.95, Wh/2 48Hz, ArH's and 1,3-diphenyl-3-methylbutan-1-one(92a) ^{1}H n.m.r. δ 1.50, C3Me, $C4H_3$; 3.27, $C2H_2$; 7.50, Wh/2 43Hz, ArH's by integration of the proton signals at δ 1.68, 2.17, 2.22 and 3.27.

Dehydration of 1,3-diphenyl-3-methylbutan-1-ol(97a)

(i) p-Toluenesulphonic acid(0.1g) was added to a solution of 1,3-diphenyl-3-methylbutan-1-ol(97a)(0.61g) in benzene and the resulting mixture heated under reflux for 6hr in a Dean and Stark apparatus[58]. After cooling, the mixture was washed with water, sodium bicarbonate solution, water and sodium chloride solution. The solution was dried over anhydrous magnesium sulphate and after the removal of solvent 3,3-dimethyl-1-phenylindane(102a)(0.59g) was isolated as a colourless oil (Found: M^+, 222.1364. $C_{17}H_{18}$ requires M^+, 222.1408). ν_{max}(neat) 755cm^{-1}. ^{1}H n.m.r. δ 1.20, C3Me; 1,38, C3Me; 2.13, Wh/2 55Hz, $C2H_2$; 4.32,

J 7.5Hz, J 10Hz, H1; 7.05, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 28.6_8, 29.0_7, C3Me; 43.0_9, C3; 49.0_0, C1; 52.7_7, C2; 121.8_1, 124.9_4, 126.2_6, 126.5_3, 126.8_8, C5, C6, C7, C8, C1para C; 128.3_8, C1ortho C, C1meta C; 145.0_9, 145.3_4, C4, C1ipso C; 152.6_6, C9.

(ii) A mixture of 1,3-diphenyl-3-methylbutan-1-ol (97a)(0.65g) and p-toluenesulphonic acid(0.11g) in benzene was heated under reflux for 0.5hr as above. The product isolated in the usual manner was 1,3-diphenyl-3-methylbut-1-ene(88a)(0.62g) (Found: M^+, 222.1377. $C_{17}H_{18}$ requires M^+, 222.1408). ν_{max}(neat) 970cm^{-1}. λ_{max} 212.5nm(ε17670), 250.5(17282), 283.5(1670), 292.5(1087). ^{1}H n.m.r. δ 1.45, C3Me, $C4H_3$; 6.36, H1, H2; 7.28, Wh/2 2Hz, ArH's. ^{13}C n.m.r. δ 125.7_2, C1; 140.0_7, C2; 40.7_2, C3; 28.7_4, C3Me, C4; 134.6_9, C1ipso C; 126.1_9, C1ortho C; 128.4_5, C1meta C; 126.9_6, C1para C; 148.6_2, C3ipso C; 126.1_9, C3ortho C; 128.1_8, C3meta C; 125.8_9, C3para C.

trans-1,3-Diphenyl-1,2-epoxy-3-methylbutane(89a)

To a solution of trans-1,3-diphenyl-3-methylbut-1-ene(88a)(3g) in ether was added m-chloroperbenzoic acid (3g)[117] and the mixture was stirred at 4°C for 4 days. Sodium bicarbonate and water were added and the resulting mixture stirred for 15min. The etheral layer was separated, washed with aqueous sodium bicarbonate and water and dried over anhydrous magnesium sulphate. After the removal of solvent the residue was absorbed onto alumina(80g). Elution with light petroleum afforded trans-1,3-diphenyl-3-methyl-but-1-ene(88a)(0.73g) ^{1}H n.m.r. δ 1.45, C3Me, $C4H_3$; 6.36, H1, H2; 7.28, Wh/2 2Hz, ArH's. Further elution with light petroleum-ether(50:1) gave trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a)(1.95g, m.p. 40-42°C) (Found: M^+, 238.1342;

C, 85.4; H, 7.7. $C_{17}H_{18}O$ requires M^+, 238.1357; C, 85.7; H, 7.6%). $\nu_{max}(CHCl_3)$ 890, 1245cm^{-1}. λ_{max} 217.5nm(ε11322), 253(440), 258(491), 261(474), 264(445), 267.5(365). ^1H n.m.r. δ 1.32, C3Me; 1.41, $C4H_3$; 3.02, J 2Hz, H2; 3.73, J 2Hz, H1; 7.32, Wh/2 8Hz, ArH's. ^{13}C n.m.r. δ 55.8_9, C1; 70.0_2, C2; 38.7_1, C3; 24.6_4, C3Me; 24.9_4, C4; 137.7_2, C1ipso C; 125.5_7, C1ortho C; 128.4_5, C1meta C; 128.0_1, C1para C; 146.5_0, C3ipso C; 126.1_0, C3ortho C; 128.3_5, C3meta C; 126.4_2, C3para C.

1-(4'-Methoxyphenyl)-3-methyl-3-phenylbutan-1-ol(97b)

A solution of 2-methyl-2-phenylprop-1-yl chloride (10g) in dry tetrahydrofuran was added to a warm suspension of magnesium(2g) in dry tetrahydrofuran and the resulting mixture was heated under reflux for 3hr. The solution was cooled in ice, under a nitrogen atmosphere and a solution of redistilled 4 -methoxybenzaldehyde(10g) in dry tetrahydrofuran was slowly added. The resulting mixture was allowed to come to room temperature over 0.5hr then water was added. The product was extracted as above. The yellow oil isolated on the removal of solvent, deposited crystals. Recrystallisation from a light petroleum-ether mixture afforded 1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-1-ol(97b)(13g, m.p. 58-60°C) (Found: M^+, 270.1563; C, 80.1; H, 8.4. $C_{18}H_{22}O_2$ requires M^+, 270.1618; C, 80.0; H, 8.2%). ν_{max}(neat) 3450cm^{-1}. ^1H n.m.r. δ 1.30, C3Me; 1.43, $C4H_3$; 1.52, OH; 2.00, Wh/2 10Hz, $C2H_2$; 3.72, ArOMe; 4.34, J 5Hz, J 8Hz, H1; 6.95, Wh/2 34Hz, ArH's. ^{13}C n.m.r. δ 71.8_2, C1; 53.7_1, C2; 37.4_5, C3; 29.3_3, C3Me; 29.7_9, C4; 55.1_7, ArOMe; 138.1_7, C1ipso C; 126.8_5, C1ortho C; 113.8_0, C1meta C; 158.7_7, C1para C; 148.8_2, C3ipso C; 125.9_7, C3ortho C; 128.2_8, C3meta C; 125.7_8, C3para C.

trans-1-(4'-Methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)

p-Toluenesulphonic acid(0.2g) was added to a solution of 1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-1-ol(97b) (1.2g) in benzene and the resulting mixture was heated under reflux, with azeotropic removal of water, for 0.25hr. The oily residue, isolated as above, was trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)(1.1g)(Found: M^+, 252.1581; C, 85.7; H, 8.2. $C_{18}H_{20}O$ requires M^+, 252.1513; C, 85.7; H, 8.0%). ν_{max}(neat) 970cm^{-1}. λ_{max} 213.5nm(ε14790), 260(17983), 263(18067), 269(15966), 274(2605), 307(1429). ^{1}H n.m.r. δ 1.50, C3Me, C4H$_3$; 3.70, ArOMe; 6.30, H1, H2; 7.05, Wh/2 32Hz, ArH's. ^{13}C n.m.r. δ 125.4$_9$, C1; 137.9$_4$, C2; 40.5$_4$, C3; 28.7$_9$, C3Me, C4; 54.9$_4$, ArOMe; 130.3$_7$, C1ipso C; 127.2$_0$, C1ortho C; 113.8$_6$, C1meta C; 158.7$_9$, C1para C; 148.8$_2$, C3ipso C; 126.1$_2$, C3ortho C; 128.0$_7$, C3meta C; 125.7$_3$, C3para C.

3,3-Dimethyl-1-(4'-methoxyphenyl)indane(102b)

p-Toluenesulphonic acid(0.7g) was added to a solution of trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene (88b)(0.2g) in benzene and the resulting mixture was heated under reflux for 4.5hr. The product isolated as above was 3,3-dimethyl-1-(4'-methoxyphenyl)indane(102b)(0.2g)(Found: M^+, 252.1564; C, 85.8; H, 8.3. $C_{18}H_{20}O$ requires M^+, 252.1513; C, 85.7; H, 8.0%). ^{1}H n.m.r. δ 1.20, 1.35, C3Me; 2.07, Wh/2 27Hz, C2H$_2$; 3.65, ArOMe; 4.27, J 8Hz, J 9Hz, H1; 6.98, Wh/2 21Hz, ArH's. ^{13}C n.m.r. δ 28.6$_4$, 28.9$_9$, C3Me; 42.8$_8$, C3; 48.1$_5$, C1; 52.8$_8$, C2; 55.0$_3$, ArOMe; 113.8$_2$, C1meta C; 121.7$_5$, 124.8$_5$, 126.4$_8$, 126.8$_1$, C5, C6, C7, C8; 129.2$_1$, C1ortho C; 137.0$_3$, C1ipso C; 145.6$_1$, C4; 152.5$_0$, C9; 158.1$_6$, C1para C.

trans-1,2-Epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b)

m-Chloroperbenzoic acid(0.4g) was added to a solution of trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene (88b)(0.64g) in ether and the resulting mixture was stirred for 4 days at 4°C. The residue isolated as above was absorbed onto alumina(80g). Elution with light petroleum gave trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)(0.13g) ^{1}H n.m.r. δ 1.50, C3Me, $C4H_3$; 3.70, ArOMe; 6.30, H1, H2; 7.05, Wh/2 32Hz, ArH's. Further elution with light petroleum-ether(50:1) afforded trans-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b)(0.37g, m.p. 62-64°C) (Found: M^+, 268.1482; C, 80.3; H, 7.7. $C_{18}H_{20}O_2$ requires M^+, 268.1462; C, 80.6, H, 7.5%). $\nu_{max}(CCl_4)$ 895, 1230cm^{-1}. λ_{max} 230nm (ε14903), 258.5(2534), 265(2743), 270.5(2864), 276(2961), 279.3(2913), 286(2403). ^{1}H n.m.r. δ 1.40, C3Me; 1.50, $C4H_3$; 3.04, J 2Hz, H2; 3.72, J 2Hz, H1; 3.77, ArOMe; 7.10, Wh/2 31Hz, ArH's. ^{13}C n.m.r. δ 55.6_6, C1; 69.6_7, C2; 38.6_2, C3; 24.5_6, C3Me; 24.8_6, C4; 55.1_2, ArOMe; 129.5_9, C1ipso C; 126.8_6, C1ortho C; 113.9_5, C1meta C; 159.5_9, C1para C; 146.5_7, C3ipso C; 126.0_6, C3ortho C; 128.3_1, C3meta C; 126.3_5, C3para C.

1-(4'-Methylphenyl)-3-methyl-3-phenylbutan-1-ol(97c)

A solution of 2-methyl-2-phenylprop-1-yl chloride (8g) in dry tetrahydrofuran was added to a warm suspension of magnesium(1.2g) in dry tetrahydrofuran and the resulting mixture was heated under reflux for 3hr. The solution was cooled in an ice-bath, under a nitrogen atmosphere,and a solution of redistilled 4 -methylbenzaldehyde(5g) in tetrahydrofuran was slowly added. The resulting mixture was allowed to come to room temperature over 0.5hr and the

solution was poured onto a saturated ammonium chloride solution. The product was extracted with ether and washed with water. The yellow oil isolated on removal of solvent deposited crystals. Recrystallisation from a light petroleum-ether mixture afforded 1-(4'-methylphenyl)-3-methyl-3-phenylbutan-1-ol(97c)(6g, m.p. 75-78°C) (Found: M^+, 254.1692. $C_{18}H_{22}O$ requires M^+, 254.1669). $\nu_{max}(CCl_4)$ 3600cm^{-1}. ^{1}H n.m.r. δ 1.28, C3Me; 1.38, $C4H_3$; 1.67, OH; 1.96, Wh/2 10Hz, $C2H_2$; 2.20, ArMe; 4.35, J 5Hz, J 8Hz, H1; 6.96, ArH's. ^{13}C n.m.r. δ 71.7_4, C1; 53.4_2, C2; 37.2_6, C3; 29.2_1, C3Me; 29.4_0, C4; 20.8_0, ArMe; 142.9_2, C1ipso C; 125.4_6, C1ortho C; 128.7_1, C1meta C; 136.2_3, C1para C; 148.6_7, C3ipso C; 125.7_4, C3ortho C; 128.0_3, C3meta C; 125.7_4, C3para C.

trans-1-(4'-Methylphenyl)-3-methyl-3-phenylbut-1-ene(88c)

p-Toluenesulphonic acid(0.4g) was added to a solution of 1-(4'-methylphenyl)-3-methyl-3-phenylbutan-1-ol(97c)(2.5g) in benzene and the resulting mixture was heated under reflux, with azeotropic removal of water, for 0.5hr. The oily residue isolated as above was trans-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(88c)(1.8g) (Found: M^+, 236.1547. $C_{18}H_{20}$ requires M^+, 236.1564). $\nu_{max}(CCl_4)$ 975cm^{-1}. λ_{max} 217nm(ε14663), 253.5(19755), 286.5(2350), 297(1442). ^{1}H n.m.r. δ 1.45, C3Me, $C4H_3$; 2.25, ArMe; 6.33, H1, H2; 7.15, Wh/2 9Hz, ArH's. ^{13}C n.m.r. δ 125.7_8, C1; 138.9_7, C2; 40.5_9, C3; 28.7_1, C3Me, C4; 21.0_2, ArMe; 134.8_4, C1ipso C; 126.0_9, C1ortho C; 129.1_2, C1meta C; 136.4_4, C1para C; 148.7_0, C3ipso C; 126.0_9, C3ortho C; 128.0_9, C3meta C; 126.0_9, C3para C.

3,3-Dimethyl-1-(4'-methylphenyl)indane(102c)

p-Toluenesulphonic acid(0.04g) was added to a solution

of trans-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(88c) (0.15g) in benzene and the resulting mixture was heated under reflux for 3.5hr. The oily residue isolated as above was absorbed onto silver nitrate alumina(13g). Elution with light petroleum-ether(50:1) afforded 3,3-dimethyl-1-(4'-methylphenyl)indane(102c)(0.045g). ^{1}H n.m.r. δ 1.22, 1.38, C3Me; 2.30, ArMe; 2.18, Wh/2 29Hz, C2H$_2$; 4.28, J 7Hz, J 11Hz, H1; 7.00, Wh/2 2Hz, ArH's. ^{13}C n.m.r. δ 21.0$_0$, ArMe; 28.6$_3$, 29.0$_1$, C3Me; 43.0$_1$, C3; 48.5$_7$, C1; 52.8$_1$, C2; 121.7$_8$, 124.9$_0$, 126.4$_7$, 126.7$_9$, C5, C6, C7, C8; 128.2$_4$, Cortho C; 129.1$_0$, Cmeta C; 135.6$_6$, Cpara C; 142.0$_1$, Cipso C; 145.5$_2$, C4; 152.6$_4$, C9.

trans-1,2-Epoxy-1-(4'-methylphenyl)-3-methyl-3-phenylbutane(89c)

m-Chloroperbenzoic acid(0.5g) was added to a solution of trans-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(88c) (1.8g) in ether and the resulting mixture was stirred for 4 days at 4°C. The residue isolated as above was absorbed onto alumina(80g). Elution with light petroleum gave trans-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(88c)(0.4g) ^{1}H n.m.r. δ 1.45, C3Me, C4H$_3$; 2.25, ArMe; 6.33, H1, H2; 7.15, Wh/2 9Hz, ArH's. Further elution with light petroleum-ether(50:1) afforded trans-1,2-epoxy-1-(4'-methylphenyl)-3-methyl-3-phenylbutane(89c)(1.3g)(Found: M$^+$, 252.1481. $C_{18}H_{20}O$ requires M$^+$, 252.1513). ν_{max}(neat) 900, 1245cm^{-1}. λ_{max} 214nm(ε11901), 223(13223), 247.5(388), 253(496), 259 (620), 261(603), 264(595), 267.5(636), 276.5(471). ^{1}H n.m.r. δ 1.26,C3Me; 1.35, C4H$_3$; 2.25, ArMe; 2.86, J 2Hz, H2; 3.58, J 2Hz, H1; 7.15, Wh/2 2Hz, ArH's. ^{13}C n.m.r. δ 69.7$_9$, C1; 55.7$_3$, C2; 38.5$_9$, C3; 24.5$_4$, C3Me; 24.8$_7$, C4; 21.0$_6$, ArMe; 134.6$_4$, Cipso C; 125.5$_1$, Cortho C; 129.1$_2$, Cmeta C;

137.6$_1$, C1para C; 146.5$_0$, C3ipso C; 126.0$_0$, C3ortho C; 128.2$_9$, C3meta C; 126.3$_3$, C3para C.

1-(4'-Chlorophenyl)-3-methyl-3-phenylbutan-1-ol(97d)

A solution of 2-methyl-2-phenylprop-1-yl chloride (5g) in dry tetrahydrofuran was added to a warm suspension of magnesium(1.8g) in dry tetrahydrofuran and the resulting mixture was heated under reflux for 3hr. The solution was cooled in ice, under a nitrogen atmosphere, and a solution of redistilled 4 -chlorobenzaldehyde(5.1g) in dry tetrahydrofuran was slowly added. The resulting mixture was allowed to come to room temperature over 0.5hr then water was added. The product was isolated by means of ether and washed with saturated sodium chloride solution. Recrystallisation of the product from a light petroleum-ether mixture afforded 1-(4'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(97d)(6.4g, m.p. 91-92^{o}C) (Found: M^+, 274.1019; C, 74.1; H, 7.3. $C_{17}H_{19}ClO$ requires M^+, 272.1122; C, 74.4; H, 7.0%). ν_{max} (CCl_4) 3450cm^{-1}. ^{1}H n.m.r. δ 1.28, C3Me; 1.38, C4H$_3$; 1.60, OH; 1.97, Wh/2 10Hz, C2H$_2$; 4.42, J 5Hz, J 8Hz, H1; 7.13, Wh/2 16Hz, ArH's. ^{13}C n.m.r. δ 71.4$_8$, C1; 53.8$_0$, C2; 37.4$_2$, C3; 29.3$_8$, C3Me' 29.5$_7$, C4; 144.2$_8$, C1ipso C; 125.9$_0$, C1ortho C; 128.3$_4$, C1meta C; 132.6$_1$, C1para C; 148.3$_6$, C3ipso C; 125.9$_0$, C3ortho C; 128.3$_4$, C3meta C; 126.9$_7$, C3para C.

trans-1-(4'-Chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)

p-Toluenesulphonic acid was added to a solution of 1-(4'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(97d)(2.8g) in benzene and the resulting mixture was heated under reflux for 0.5hr. The product isolated as above was trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(2.4g)(Found:

M^+, 256.1056; C, 80.0; H, 6.5. $C_{17}H_{17}Cl$ requires M^+, 256.1017; C, 79.7, H, 6.7%). ν_{max}(neat) 970cm^{-1}. λ_{max} 212.5nm(ε25641), 257(30769), 290(3017), 300(1659). ^{1}H n.m.r. δ 1.47, C3Me, $C4H_3$; 6.33, H1, H2; 7.22, Wh/2 2Hz, ArH's. ^{13}C n.m.r. δ 124.9_5, C1; 140.7_8, C2; 40.6_9, C3; 28.5_8, C3Me, C4; 136.1_4, C1ipso C; 127.3_1, C1ortho C; 128.5_3, C1meta C; 132.4_8, C1para C; 148.3_0, C3ipso C; 126.0_9, C3ortho C; 128.1_9, C3meta C; 125.9_4, C3para C.

1-(4'-Chlorophenyl)-3,3-dimethylindane(102d)

p-Toluenesulphonic acid(0.1g) was added to a solution of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d) (0.35g) in benzene and the resulting mixture was heated under reflux for 13hr. The residue, isolated as above, was absorbed onto silver nitrate alumina(13g). Elution with light petroleum-ether(50:1) afforded 1-(4'-chlorophenyl)-3,3-dimethylindane(102d)(0.063g) (Found: M^+, 256.1099; C, 80.2, H, 6.7. $C_{17}H_{17}Cl$ requires M^+, 256.1017; C, 79.7; H, 6.7%). ^{1}H n.m.r. δ 1.12, 1,40, C3Me; 2.05, Wh/2 35Hz, $C2H_2$; 4.35, J 8Hz, J 10Hz, H1; 7.10, Wh/2 4Hz, ArH's. ^{13}C n.m.r. δ 29.0_2, 29.7_4, C3Me; 43.1_4, C3; 48.4_4, C1; 52.7_4, C2; 121.9_8, 124.8_1, 126.6_3, 127.1_0, C5, C6, C7, C8; 128.5_6, C1meta C; 129.7_3, C1ortho C; 132.0_3, C1para C; 143.6_5, C1ipso C; 144.8_0, C4; 152.6_9, C9. Further elution with light petroleum-ether(20:1) gave trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(0.14g) ^{1}H n.m.r. δ 1.47, C3Me, $C4H_3$; 6.33, H1, H2; 7.22, Wh/2 2Hz, ArH's.

trans-1-(4'-Chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89d)

m-Chloroperbenzoic acid(0.35g) was added to a solution of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1ene(88d)

(0.6g) in ether and the resulting mixture was stirred for 4 days at 4°C. The residue, isolated as above, was absorbed onto alumina(80g). Elution with light petroleum-ether(50:1) gave trans-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89d)(0.58g, m.p. 28-30°C) (Found: M^+, 272.1064; C, 74.9; H, 6.3. $C_{17}H_{17}O$ requires M^+, 272.0966; C, 75.0; H, 6.3%). ν_{max}(neat) 895cm^{-1}. λ_{max}231nm(ε11792), 252.2(2581), 257.7(3118), 263.7(3262), 270.5(2724), 279.5(1935). ^{1}H n.m.r. δ 1.25, C3Me; 1.35, $C4H_3$; 2.81, J 2Hz, H2; 3.55, J 2Hz, H1; 7.15, Wh/2 7Hz, ArH's. ^{13}C n.m.r. δ 55.2_2, C1; 70.1_5, C2; 38.6_5, C3; 24.5_5, C3Me; 24.8_9, C4; 136.2_7, C1ipso C; 126.8_4; C1ortho C; 128.3_6, C1meta C; 133.7_8, C1para C; 146.1_8, C3ipso C; 126.0_1, C3ortho C; 128.6_5, C3meta C; 126.4_9, C3para C.

1-(3'-Chlorophenyl)-3-methyl-3-phenylbutan-1-ol(97e)

A solution of 2-methyl-2-phenylprop-1-yl chloride (12g) in dry tetrahydrofuran was added to a warm suspension of magnesium(2.5g) in dry tetrahydrofuran and the resulting mixture was heated under reflux for 3hr. The solution was cooled in ice, under a nitrogen atmosphere, and a solution of redistilled 3 -chlorobenzaldehyde(12g) in dry tetrahydrofuran was slowly added. The resulting mixture was allowed to come to room temperature over 0.5hr and water was added. The yellow oil, isolated as above, was absorbed onto alumina (160g). Elution with light petroleum-ether(20:1) afforded 1-(3'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(97e)(6.8g, m.p. 101-103°C) (Found: M^+, 274.1063; C, 74.5; H, 7.0. $C_{17}H_{19}ClO$ requires M^+, 274.1122; C, 74.4; H, 7.0%). ν_{max} (neat) 3375cm^{-1}. ^{1}H n.m.r. δ 1.25, C3Me; 1.37, $C4H_3$; 1.72, OH; 1.87, Wh/2 9Hz, $C2H_2$; 4.27, J 5Hz, J 7Hz, H1; 7.01, Wh/2 15 Hz, ArH's. ^{13}C n.m.r. δ 71.5_5, C1; 53.7_8, C2;

37.4_3, C3; 29.4_4, C3Me, C4; 147.9_7, ClC$_1$; 125.9_1, ClC$_2$; 134.0_9, ClC$_3$; 127.1_2, ClC$_4$; 129.5_1, ClC$_5$; 123.7_0, ClC$_6$; 148.3_1, C3ipso C; 125.9_1, C3ortho C; 128.3_4, C3meta C; 125.8_1, C3para C.

trans-1-(3'-Chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)

p-Toluenesulphonic acid(0.12g) was added to a solution of 1-(3'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(97e) (0.86g) in benzene and the resulting mixture was heated under reflux, with azeotropic removal of water, for 0.5hr. The oily residue, isolated as above, was trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)(0.58g) (Found: M^+, 256.0939; C, 80.0; H, 6.6. $C_{17}H_{17}Cl$ requires M^+, 256.1017; C, 79.7; H, 6.7%). ν_{max}(neat) 970cm^{-1}. λ_{max} 220nm(ε20752), 252.5(20075), 291(1466), 300.5(1030). ^{1}H n.m.r. δ 1.45, C3Me, C4H$_3$; 6.30, H1, H2; 7.10, Wh/2 12Hz, ArH's. ^{13}C n.m.r. δ 124.9_3, C1; 141.6_4, C2; 40.7_7, C3; 28.5_6, C3Me, C4; 139.6_0, ClC$_1$; 126.8_5, ClC$_2$; 134.3_7, ClC$_3$; 126.8_5, ClC$_4$; 129.5_9, ClC$_5$; 124.3_7, ClC$_6$; 148.1_4, C3ipso C; 126.0_6, C3ortho C; 128.2_1, C3meta C; 125.9_9, C3para C.

1-(3'-Chlorophenyl)-3,3-dimethylindane(102e)

p-Toluenesulphonic acid(0.1g) was added to a solution of trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e) (0.37g) in benzene and the resulting mixture was heated under reflux for 22hr. The oily residue, isolated as above, was 1-(3'-chlorophenyl)-3,3-dimethylindane(102e)(0.35g) ^{1}H n.m.r. δ 1.20, 1.37, C3Me; 2.23, Wh/2 32Hz, C2H$_2$; 4.37, J 7Hz, J 10Hz, H1; 7.20, Wh/2 6Hz, ArH's. ^{13}C n.m.r. δ 28.5_7, 29.0_1, C3Me; 43.0_8, C3; 48.8_9, C1; 52.5_4, C2; 121.9_2, 124.8_0, 126.4_3, 126.5_7, 127.1_0, C5, C6, C7, C8, ClC$_6$; 127.8_9, ClC$_4$; 128.4_2, ClC$_2$; 129.6_0, ClC$_5$; 134.2_3, ClC$_3$; 144.3_8, C4;

147.2$_8$, Cl$\underline{C}_1$; 152.5$_9$, C9.

trans-1-(3'-Chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89e)

m-Chloroperbenzoic acid(0.2g) was added to a solution of trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e) (0.4g) in ether and the resulting mixture was stirred for 7 days at 4°C. The residue, isolated as above, was absorbed onto an alumina dry column(20g). A light petroleum-ether solution(50:1) was allowed to percolate through the column. Elution of segment c. Rf 1 to 0.5 with ether gave trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)(0.03g) ^{1}H n.m.r. δ 1.45, C3Me, C4H$_3$; 6.20, H1, H2; 7.10, Wh/2 12Hz, ArH's. Elution of segment c. Rf 0.5 to 0.15 with ether afforded trans-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89e)(0.20g) (Found: M$^+$, 272.0793; C, 75.4; H, 6.2. $C_{17}H_{17}ClO$ requires M$^+$, 272.0966; C, 75.0; H, 6.3%). ν_{max}(neat) 880cm^{-1}. λ_{max} 232nm(ε9547), 244(7657), 256.3 (7632), 263.2(6927). ^{1}H n.m.r. δ 1.28, C3Me; 1.35, C4H$_3$; 2.94, J 2Hz, H2; 3.64, J 2Hz, H1; 7.15, Wh/2 14Hz, ArH's. ^{13}C n.m.r. δ 54.9$_7$, C1; 70.0$_3$, C2; 38.5$_1$, C3; 24.4$_9$, C3Me; 24.7$_8$, C4; 139.9$_8$, Cl$\underline{C}_1$; 125.4$_8$, Cl$\underline{C}_2$; 134.4$_6$, Cl$\underline{C}_3$; 128.3$_1$, Cl$\underline{C}_4$; 129.6$_2$, Cl$\underline{C}_5$; 123.6$_2$, Cl$\underline{C}_6$; 146.0$_3$, C3ipso C; 125.9$_3$; C3ortho C; 128.3$_1$, C3meta C; 126.4$_1$, C3para C.

1-(3',4'-Dichlorophenyl)-3-methyl-3-phenylbutan-1-ol(97f)

A solution of 2-methyl-2-phenylprop-1-yl chloride (8g) in dry tetrahydrofuran was added to a warm suspension of magnesium(1.2g) in dry tetrahydrofuran and the resulting mixture was heated under reflux for 3hr. The solution was cooled in ice, under a nitrogen atmosphere, and a solution of 3 ,4 -dichlorobenzaldehyde(7g) in dry tetrahydrofuran was slowly added. The resulting mixture was allowed to

come to room temperature over 1hr. The oily residue,isolated as above, was absorbed onto alumina(160g). Elution with light petroleum-ether(20:1) afforded 1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbutan-1-ol(97f)(6g). ν_{max}(neat) 3450cm^{-1}. ^{1}H n.m.r. δ 1.33, C3Me; 1.40, C4H$_3$; 1.70, OH; 1.97, Wh/2 10Hz, C2H$_2$; 4.40, J 5Hz, J 7Hz, H1; 7.10, Wh/2 10Hz, ArH's. ^{13}C n.m.r. δ 70.9$_2$, C1; 53.7$_3$, C2; 37.3$_2$, C3; 29.3$_8$, C3Me, C4; 145.9$_0$, ClC$_1$; 127.5$_5$, ClC$_2$; 132.1$_8$, ClC$_3$; 130.6$_7$, ClC$_4$; 130.0$_4$, ClC$_5$; 124.8$_1$, ClC$_6$; 147.9$_1$, C3ipso C; 125.7$_9$, C3ortho C; 128.3$_3$, C3meta C; 125.9$_8$, C3para C.

trans-1-(3',4'-Dichlorophenyl)-3-methyl-3-phenylbut-1-ene(88f)

p-Toluenesulphonic acid(0.5g) was added to a solution of 1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbutan-1-ol (97f)(3g) in benzene and the resulting mixture was heated under reflux, with azeotropic removal of water, for 1hr. The oily residue, isolated as above, was absorbed onto alumina(80g). Elution with light petroleum gave trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(88f) (2.1g) (Found: M$^+$, 290.0625. $C_{17}H_{17}Cl_2$ requires M$^+$, 290.0626). ν_{max}(neat) 970cm^{-1}. λ_{max} 220.5nm(ε25877), 259(22975), 264.5(22007), 270(18380), 297(1935), 308(1270). ^{1}H n.m.r. δ 1.45, C3Me, C4H$_3$; 6.19, J 16Hz, H2; 6.34, J 16Hz, H1; 7.20, Wh/2 2Hz, ArH's. ^{13}C n.m.r. δ 123.9$_2$, C1; 142.0$_8$, C2; 40.6$_7$, C3; 28.4$_0$, C3Me, C4; 137.6$_9$, ClC$_1$; 127.7$_3$, ClC$_2$; 132.3$_9$, ClC$_3$; 130.3$_5$, ClC$_4$; 130.1$_0$, ClC$_5$; 125.2$_1$, ClC$_6$; 147.7$_9$, C3ipso C; 126.0$_1$, C3ortho C; 128.1$_9$, C3meta C; 126.0$_1$, C3para C.

1-(3',4'-Dichlorophenyl)-3,3-dimethylindane(102f)

p-Toluenesulphonic acid was added to a solution of trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-

ene(88f)(0.2g) in benzene and the resulting mixture was heated under reflux for 18hr. The oily residue, isolated as above, was absorbed onto silver nitrate alumina(15g). Elution with light petroleum afforded 1-(3',4'-dichlorophenyl)-3,3-dimethylindane(102f)(0.081g). ^{1}H n.m.r. δ 1.23, 1.40, C3Me; 2.12, Wh/2 32Hz, C2H$_2$; 4.19, J 7Hz, J10Hz, H1; 7.17, Wh/2 9Hz, ArH's. ^{13}C n.m.r. δ 28.5$_9$, 29.0$_2$, C3Me; 43.2$_0$, C3; 48.2$_7$, C1; 52.5$_8$, C2; 122.0$_9$, 124.7$_5$, 126.5$_4$, 126.7$_9$, C5, C6, C7, C8; 128.2$_9$, ClC$_6$; 130.3$_5$, 130.7$_9$, ClC$_2$; ClC$_5$; 144.0$_6$, C4; 145.5$_7$, ClC$_1$; 152.7$_1$, C9. Further elution gave trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(88f)(0.117g) ^{1}H n.m.r. δ 1.45, C3Me, C4H$_3$; 6.19, J 16Hz, H2; 6.34, J 16Hz, H1; 7.20, Wh/2 2Hz, ArH's.

trans-1-(3',4'-Dichlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89f)

m-Chloroperbenzoic acid(0.6g) was added to a solution of trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(88f)(1.6g) and the resulting mixture was stirred for 6 days at 4^{o}C. The residue, isolated as above, was absorbed onto alumina(80g). Elution with light petroleum gave trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(88f) (0.80g) ^{1}H n.m.r. δ 1.45, C3Me, C4H$_3$; 6.19, J 16Hz, H2; 6.34, J 16Hz, H1; 7.2, Wh/2 2Hz, ArH's. Further elution with light petroleum-ether(50:1) afforded trans-1-(3',4'-dichlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89f) (0.63g) (Found: M$^+$, 306.0553. $C_{17}H_{16}Cl_2O$ requires M$^+$, 306.0576). ν_{max}(CCl_4) 880cm^{-1}. λ_{max} 211.5nm(ε25898), 231.2 (12665), 258(671), 277.5(756), 286(662). ^{1}H n.m.r. δ 1.31, C3Me; 1.39, C4H$_3$; 2.93, J 1.5Hz, H2; 3.63, J 1.5Hz, H1; 7.20, Wh/2 7Hz, ArH's. ^{13}C n.m.r. δ 70.2$_6$, C1; 54.5$_8$, C2; 38.5$_7$, C3; 24.5$_0$, C3Me; 24.8$_0$, C4; 138.1$_7$, ClC$_1$; 127.3$_8$,

ClC_2; 132.7_5, ClC_3; 131.8_7, ClC_4; 130.4_2, ClC_5; 124.8_0, ClC_6; 145.8_9, C3ipso C; 125.9_7, C3ortho C; 128.3_6, C3meta C; 126.5_4, C3para C.

trans-1-(4'-Cyanophenyl)-3-methyl-3-phenylbut-1-ene(88g)

Cuprous cyanide(6.0g) was added to a solution of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d) (2.0g) in N-methyl-2-pyrrolidone(35ml) and the resulting mixture was heated under reflux, with stirring, for 44hr then cooled[75]. The solution was poured into ethylenediamine (75ml) and allowed to stand for 2hr. The mixture was poured onto ice water(0.5l) and the product extracted with ether. The solvent was removed and the residue was absorbed onto alumina(80g). Elution with light petroleum gave trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(0.44g) ^{1}H n.m.r. δ 1.47, C3Me, $C4H_3$; 6.33, H1, H2; 7.22, Wh/2 2Hz, ArH's. Further elution with light petroleum-ether(50:1) afforded trans-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(88g)(0.25g) (Found: M^+, 247.1353. $C_{18}H_{17}N$ requires M^+, 247.1366). $\nu_{max}(CCl_4)$ 970, 2220cm^{-1}. λ_{max} 213.5nm (ε20033), 275.5(32053), 301(5342). ^{1}H n.m.r. δ 1.52, C3Me, $C4H_3$; 6.34, J 16Hz, H2; 6.52, J 16Hz, H1; 7.37, Wh/2 13Hz, ArH's. ^{13}C n.m.r. δ 124.8_3, C1; 144.2_1, C2; 41.0_0, C3; 28.4_2, C3Me, C4; 118.9_3, ArCN; 142.1_7, C1ipso C; 126.6_4, C1ortho C; 132.2_5, C1meta C; 110.1_4, C1para C; 147.7_4, C3ipso C; 126.1_2, C3ortho C; 128.3_1, C3meta C; 126.6_4, C3para C.

Photolysis of trans-1,3-diphenyl-3-methylbut-1-ene(88a)

(i) A solution of trans-1,3-diphenyl-3-methylbut-1-ene(88a)(0.107g) in anhydrous deoxygenated t-butyl alcohol (150ml) in a quartz vessel under a nitrogen atmosphere, was irradiated(2537Å) for 6hr and the reaction was monitored by g.l.c. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-3,3-dimethyl-1,2-diphenylcyclopropane(112a)(71%) and 3,4-diphenyl-2-methylbut-1-ene(115a)(29%). The residue was absorbed onto silver nitrate alumina(13g). Elution with light petroleum-ether(50:1) afforded trans-3,3-dimethyl-1,2-diphenylcyclopropane(112a)(0.059g)(Found: M^+, 222.1413. $C_{17}H_{18}$ requires M^+, 222.1408). $\nu_{max}(CCl_4)$ 1025cm^{-1}. λ_{max} 212.5nm(ε16154), 223(18702), 252.5(2115), 265(1587), 275 (577), 284.5(192), 293(125). ^{1}H n.m.r. δ 0.96, C3Me; 2.37, H1, H2; 7.28, ArH's. ^{13}C n.m.r. δ 34.4_2, C1, C2; 25.8_2, C3; 22.3_1, C3Me; 139.7_4, C1-, C2ipso C; 129.0_9, C1-, C2ortho C; 128.0_7, C1-, C2meta C; 125.9_1, C1-, C2para C.

Further elution with light petroleum-ether(5:1) gave 3,4-diphenyl-2-methylbut-1-ene(115a)(0.025g) (Found: M^+, 222.1395; C, 91.9; H, 8.5. $C_{17}H_{18}$ requires M^+, 222.1408; C, 91.8; H, 8.2%). $\nu_{max}(CCl_4)$ 890, 1645cm^{-1}. ^{1}H n.m.r. δ 1.60, C2Me; 3.28, Wh/2 27Hz, H3, $C4H_2$; 4.88, Wh/2 8Hz, $C1H_2$; 7.10, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 110.8_6, C1; 147.3_8, C2; 54.4_7, C3; 39.9_6, C4; 21.5_0, C2Me; 142.9_0, C3ipso C; 128.1_4, C3ortho C; 128.0_0, C3meta C; 126.2_5, C3para C; 140.5_8; C4ipso C; 129.9_8, C4ortho C; 128.0_0, C4meta C; 125.7_6, C4para C.

(ii) A solution of trans-1,3-diphenyl-3-methyl-but-1-ene(88a)(0.097g) in anhydrous deoxygenated t-butyl alcohol(150ml) was irradiated(2537Å) in a quartz vessel

under a nitrogen atmosphere for 0.25hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1,3-diphenyl-3-methylbut-1-ene(88a)(67%) ^{1}H n.m.r. δ 1.45, C3Me, C4H$_3$; 6.36, H1, H2; 7.28, ArH's, cis-1,3-diphenyl-3-methylbut-1-ene(109a)(4%) ^{1}H n.m.r. δ 1.33, C3Me, C4H$_3$; 5.79, J 13Hz, H2; 6.39, J 13Hz, H1; 7.05, ArH's and trans-3,3-dimethyl-1,2-diphenylcyclopropane(112a)(29%) ^{1}H n.m.r. δ 0.96, C3Me; 2.37, H1, H2; 7.28, ArH's. The ratio of the products was determined by integration of the peaks at δ 0.96, 1.33 and 1.45 respectively.

The product was taken up in anhydrous t-butyl alcohol (150ml), the solution deoxygenated and irradiated for a further 0.25hr. After the removal of the solvent analysis of the residue by ^{1}H n.m.r. spectroscopy showed the presence of trans-1,3-diphenyl-3-methylbut-1-ene(88a)(32%), cis-1,3-diphenyl-3-methylbut-1-ene(109a)(4%) and trans-3,3-dimethyl-1,2-diphenylcyclopropane(112a)(64%) by integration of the peaks at δ 0.96, 1.33 and 1.45 respectively.

(iii) A solution of trans-1,3-diphenyl-3-methylbut-1-ene(88a)(0.126g) in anhydrous deoxgenated benzene(150ml) in a quartz vessel under a nitrogen atmosphere, was irradiated (2537Å) for 6hr and the reaction was monitored by g.l.c. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-3,3-dimethyl-1,2-diphenylcyclopropane(112a)(50%) and 3,4-diphenyl-2-methylbut-1-ene(115a)(50%). The residue was absorbed onto silver nitrate alumina(13g). Elution with light petroleum-ether(50:1) gave trans-3,3-dimethyl-1,2-diphenylcyclopropane (112a)(0.062g) ^{1}H n.m.r. δ 0.96, C3Me; 2.37, H1, H2; 7.28, ArH's. Further elution with light petroleum-ether(5:1)

afforded 3,4-diphenyl-2-methylbut-1-ene(115a)(0.040g) ^{1}H n.m.r. δ 1.60, C2Me; 3.28, Wh/2 27Hz, H3, C4H$_2$; 4.88, Wh/2 8Hz, C1H$_2$; 7.10, Wh/2 3Hz, ArH's.

Photolysis of trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)

(i) A solution of trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)(0.108g) in anhydrous deoxygenated t-butyl alcohol(150ml) was irradiated(2537Å) as above for 6hr and the reaction was followed by g.l.c. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)(33%), cis-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(109b)(56%) and trans-3,3-dimethyl-1-(4'-methoxyphenyl)-2-phenylcyclopropane(112b)(11%). The residue was absorbed onto silver nitrate alumina(13g). Elution with light petroleum-ether(20:1) afforded trans-3,3-dimethyl-1-(4'-methoxyphenyl)-2-phenylcyclopropane(112b)(c. 0.008g) ^{1}H n.m.r. δ 0.95, C3Me; 2.30, H1, H2; 3.78, ArOMe; 7.02, ArH's.

Further elution with light petroleum-ether(5:1) gave cis-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(109b)(0.048g, m.p. 44-45^{0}C) (Found: M$^+$, 252.1581; C, 85.7; H,8.2. $C_{18}H_{20}O$ requires M$^+$, 252.1513; C, 85.7; H, 8.0%). $\nu_{max}(CCl_4)$ 705cm^{-1}. ^{1}H n.m.r. δ 1.38, C3Me, C4H$_3$; 3.71, ArOMe; 5.83, J 13Hz, H2; 6.41, J 13Hz, H1; 6.90, Wh/2 40Hz, ArH's. ^{13}C n.m.r. δ 125.4$_9$, C1; 140.5$_8$, C2; 40.7$_8$, C3; 31.1$_6$, C3Me, C4; 55.0$_3$, ArOMe; 130.0$_7$, C1ipso C, C1ortho C; 112.8$_9$, C1meta C; 158.0$_1$, C1para C; 150.1$_4$, C3ipso C; 128.1$_2$, C3ortho C; 128.4$_7$, C3meta C; 126.0$_2$, C3para C. Further elution afforded trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)(0.028g) ^{1}H n.m.r. δ 1.50, C3Me, C4H$_3$;

3.70, ArOMe; 6.30, H1, H2; 7.05, Wh/2 32Hz, ArH's.

(ii) A solution of trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)(0.110g) in anhydrous deoxygenated t-butyl alcohol(150ml) was irradiated(2537Å) as above for 0.25hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b) (75%) ^{1}H n.m.r. δ 1.50, C3Me, C4H$_3$; 3.70, ArOMe; 6.30, H1, H2; 7.05, Wh/2 32Hz, ArH's and cis-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(109b)(25%) ^{1}H n.m.r. δ 1.38, C3Me, C4H$_3$; 3.71, ArOMe; 5.83, J 13Hz, H2; 6.41, J 13Hz, H1; 6.90, Wh/2 40Hz, ArH's.

The product was taken up in anhydrous t-butyl alcohol (150ml), the solution deoxygenated and irradiated for a further 0.25hr. After the removal of the solvent, analysis of the residue by ^{1}H n.m.r. showed the presence of trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)(67%) cis-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(109b) (31%) and trans-3,3-dimethyl-1-(4'-methoxyphenyl)-2-phenylcyclopropane(112b)(2%) ^{1}H n.m.r. δ 0.95, C3Me; 2.30, H1, H2; 3.78, ArOMe; 7.02, ArH'S, by integration of the peaks at δ 1.50, 1.38 and 0.95 respectively.

(iii) A solution of trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)(0.100g) in anhydrous deoxygenated benzene(150ml) was irradiated(2537Å) as above for 6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)(66%), cis-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(109b) (28%) and trans-3,3-dimethyl-1-(4'-methoxyphenyl)-2-phenylcyclopropane(112b)(6%). The residue was absorbed onto silver

nitrate alumina(13g). Elution with light petroleum-ether (20:1) afforded trans-3,3-dimethyl-1-(4'-methoxyphenyl)-2-phenylcyclopropane(112b)(c. 0.005g) ^{1}H n.m.r. δ 0.95, C3Me; 2.30, H1, H2; 3.78, ArOMe; 7.02, ArH's. Further elution with light petroleum-ether(5:1) gave cis-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(109b)(0.028g) ^{1}H n.m.r. δ 1.38, C3Me, C4H$_3$; 3.71, ArOMe; 5.83, J 13Hz, H2; 6.41, J 13Hz, H1; 6.90, Wh/2 40Hz, ArH's and trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)(0.039g) ^{1}H n.m.r. δ 1.50, C3Me, C4H$_3$; 3.70, ArOMe; 6.30, H1, H2; 7.05, Wh/2 32Hz, ArH's.

Photolysis of trans-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(88c)

(i) A solution of trans-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(88c)(0.121g) in anhydrous deoxygenated t-butyl alcohol(120ml) was irradiated(2537Å) as above for 6 hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(88c)(0.5%) ^{1}H n.m.r. δ 1.45, C3Me, C4H$_2$; 2.25, ArMe; 6.33, H1, H2; 7.15, Wh/2 9Hz, ArH's, cis-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(109c)(0.5%) ^{1}H n.m.r. δ 1.33, C3Me, C4H$_3$; 2.25, ArMe; 5.81, J 12Hz, H2; 6.40, J 12Hz, H1; 7.20, ArH's, trans-3,3-dimethyl-1-(4'-methylphenyl)-2-phenylcyclopropane (112c)(88%) and 4-(4'-methylphenyl)-2-methyl-3-phenylbut-1-ene(115c)(11%).

The residue was absorbed onto silver nitrate alumina (13g). Elution with light petroleum-ether(50:1) afforded trans-3,3-dimethyl-1-(4'-methylphenyl)-2-phenylcyclopropane(112c)(0.103g) ν_{max}(CCl$_4$) 1450cm^{-1}. ^{1}H n.m.r. δ 0.97, C3Me; 2.30, ArMe, H1, H2; 7.08, C2ArH's; 7.20, C1ArH's.

^{13}C n.m.r. δ 33.9_8, C1; 34.3_4, C2; 25.6_6, C3; 22.2_9, C3Me; 21.0_6, ArMe; 136.5_3, C1ipso C; 128.9_1, C1ortho C; 128.7_6, C1meta C; 135.3_1, C1para C; 139.8_1, C2ipso C; 129.0_6, C2ortho C; 127.9_8, C2meta C; 125.7_9, C2para C.

Further elution with light petroleum-ether(5:1) afforded 4-(4'-methylphenyl)-2-methyl-3-phenylbut-1-ene (115c)(0.013g). $\nu_{max}(CCl_4)$ 890cm^{-1}. ^1H n.m.r. δ 1.60, C2Me; 2.26, ArMe; 3.42, Wh/2 30Hz, H3, C4H_2; 4.85, Wh/2 9Hz, C1H_2; 6.90, C4ArH's; 7.16, C3ArH's. ^{13}C n.m.r. δ 110.8_3, C1; 147.4_2, C2; 54.4_9, C3; 39.4_5, C4; 21.4_8, C2Me; 21.0_0; ArMe; 143.0_6, C3ipso C; 128.1_2, C3ortho C; 128.0_1, C3meta C; 126.1_8, C3para C; 137.4_4, C4ipso C; 128.8_1, C4ortho C; 128.7_1, C4meta C; 135.1_0, C4para C.

(ii) A solution of trans-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(88c)(0.107g) in anhydrous deoxygenated t-butyl alcohol(150ml) was irradiated as above for 0.25hr. The solvent was removed and the ^1H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(88c)(76%) ^1H n.m.r. δ 1.45, C3Me, C4H_3; 2.25, ArMe; 6.33, H1, H2; 7.15, ArH'S, cis-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(109c) (6%) ^1H n.m.r. δ 1.33, C3Me, C4H_3; 2,25, ArMe; 5.81, J 12Hz, H2; 6.40, J 12Hz, H1; 7.20, ArH's and trans-3,3-dimethyl-1-(4'-methylphenyl)-2-phenylcyclopropane(112c)(19%) ^1H n.m.r. δ 0.97, C3Me; 2.30, ArMe, H1, H2; 7.08, C2ArH's; 7.20, C1ArH's.

The product was taken up in anhydrous t-butyl alcohol (150ml), the solution deoxygenated and irradiated for a further 0.25hr. After the removal of solvent, analysis by ^1H n.m.r. showed the presence of trans-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(88c)(57%), cis-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(109c)(12%) and trans-

3,3-dimethyl-1-(4'-methylphenyl)-2-phenylcyclopropane(112c) (31%) by integration of the peaks at δ 1.45, 1.33 and 0.97 respectively.

(iii) A solution of trans-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(88c)(0.122g) in anhydrous deoxygenated benzene(120ml) was irradiated as above for 6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-3,3-dimethyl-1-(4'-methylphenyl)-2-phenylcyclopropane(112c)(67%) and 4-(4'-methylphenyl)-2-methyl-3-phenylbut-1-ene(115c)(33%). The residue was absorbed onto silver nitrate alumina(13g). Elution with light petroleum-ether(50:1) afforded trans-3,3-dimethyl-1-(4'-methylphenyl)-2-phenylcyclopropane(112c) (0.082g) ^{1}H n.m.r. δ 0.97, C3Me; 2.30, ArMe, H1, H2; 7.08, C2ArH's; 7.20, ClArH's. Further elution with light petroleum-ether(5:1) gave 4-(4'-methylphenyl)-2-methyl-3-phenylbut-1-ene(115c)(0.027g) ^{1}H n.m.r. δ 1.60, C2Me; 2.26, ArMe; 3.42, Wh/2 30Hz, H3, $C4H_2$; 4.85, Wh/2 9Hz, ClH_2; 6.90, C4ArH's; 7.16, C3ArH's.

Photolysis of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)

(i) A solution of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(0.115g) in anhydrous deoxygenated t-butyl alcohol(150ml) was irradiated(2537Å) as above for 6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(11%), cis-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(109d)(30%), trans-1-(4'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane (112d)(55%) and 4-(4'-chlorophenyl)-2-methyl-3-phenylbut-1-ene(115d)(4%).

The residue was absorbed onto silver nitrate alumina (13g). Elution with light petroleum-ether(50:1) gave trans-1-(4'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112d) (0.052g) (Found: M^+, 256.1019; C, 79.9; H, 6.5. $C_{17}H_{17}Cl$ requires M^+, 256.1017; C, 79.7; H,6.7%). ν_{max} (CCl_4) 1010cm^{-1}. λ_{max} 210.5(ε13273), 220.5(11955), 229.5(12500) 257.5(6682), 290(636), 301(325). ^1H n.m.r. δ 0.96, C3Me; 2.31, H1, H2; 7.23, Wh/2 4Hz, ArH's. ^{13}C n.m.r. δ 33.6_9, C1; 34.6_5, C2; 25.9_5, C3; 22.2_0, C3Me; 22.3_1, C3Me; 138.2_6, C1ipso C; 130.4_0, C1ortho C; 128.2_0, C1meta C; 131.6_7, C1para C; 139.2_8, C2ipso C; 129.0_1, C2ortho C; 128.1_0, C2meta C; 126.0_6, C2para C.

Elution with light petroleum-ether(20:1) afforded cis-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(109d) (0.028g) (Found: M^+, 256.1079; C, 79.8; H, 6.7. $C_{17}H_{17}Cl$ requires M^+, 256.1017; C, 79.7, H, 6.7%). ν_{max}(CCl_4) 710cm^{-1}. ^1H n.m.r. δ 1.36, C3Me, $C4H_3$; 5.92, J 12Hz, H2; 6.41, J 12Hz, H1; 7.03, Wh/2 4Hz, ArH's. ^{13}C n.m.r. δ 126.1_6, C1; 140.9_1, C2; 40.8_6, C3; 31.1_2, C3Me, C4; 136.3_6, C1ipso C; 127.5_4, C1ortho C; 128.2_6, C1meta C; 130.1_6, C1para C; 142.5_0, C3ipso C; 126.0_6, C3ortho C; 128.6_5, C3meta C; 125.6_7, C3para C. Further elution gave trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(0.010g) ^1H n.m.r. δ 1.47, C3Me, $C4H_3$; 6.33, H1, H2; 7.22, ArH's.

Elution with light petroleum-ether(5:1) afforded 4-(4'-chlorophenyl)-2-methyl-3-phenylbut-1-ene(115d)(0.004g) (Found: M^+, 256.0985; C, 80.0; H, 7.0. $C_{17}H_{17}Cl$ requires M^+, 256.1017; C, 79.7; H, 6.7%). ν_{max}(CCl_4) 890, 1640cm^{-1}. ^1H n.m.r. δ 1.60, C2Me; 3.24, Wh/2 27Hz, H3, $C4H_2$; 4.90, Wh/2 6Hz, $C1H_2$; 7.02, Wh/2 11Hz, ArH's. ^{13}C n.m.r. δ 110.9_1, C1; 147.1_6, C2; 54.5_8, C3; 39.4_1, C4; 21.5_9, C2Me; 142.4_9, C3ipso C; 128.1_3, C3ortho C; 127.9_8, C3meta C; 126.4_2,

C3para C; 139.0_6, C4ipso C; 130.3_2, C4ortho C; 128.2_2, C4meta C; 131.5_9, C4para C.

(ii) A solution of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(0.103g) in anhydrous deoxygenated t-butyl alcohol(150ml) was irradiated as above for 0.25hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(74%) ^{1}H n.m.r. δ 1.47, C3Me, $C4H_3$; 6.33, H1, H2; 7.22, ArH's, cis-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(109d)(22%) ^{1}H n.m.r. δ 1.36, C3Me, $C4H_3$; 5.92, J 12Hz, H2; 6.41, J 12Hz, H1; 7.03, ArH's and trans-1-(4'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112d)(4%) ^{1}H n.m.r. δ 0.96, C3Me; 2.31, H1, H2; 7.23, ArH's.

The product was taken up in anhydrous t-butyl alcohol (150ml), the solution deoxygenated and irradiated for a further 0.25hr. After the removal of solvent, analysis of the residue by ^{1}H n.m.r. showed the presence of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(55%), cis-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(109d)(34%) and trans-1-(4'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112d)(11%) by integration of the peaks at δ 1.47, 1.36 and 0.96 respectively.

(iii) A solution of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(0.108g) in anhydrous deoxygenated benzene(150ml) was irradiated(2537Å) as above for 6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(16%), cis-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(109d)(22%), trans-1-(4'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112d)

(38%) and 4-(4'-chlorophenyl)-2-methyl-3-phenylbut-1-ene (115d)(24%). The residue was absorbed onto silver nitrate alumina(13g). Elution with light petroleum-ether(50:1) gave trans-1-(4'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane (112d)(0.041g) ^{1}H n.m.r. δ 0.96, C3Me; 2.31, H1, H2; 7.23, ArH's. Further elution with light petroleum-ether(20:1) afforded cis-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene (109d)(0.007g) ^{1}H n.m.r. δ 1.36, C3Me, $C4H_3$; 5.92, J 12Hz, H2; 6.41, J 12Hz, H1; 7.03, ArH's and trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(0.015g) ^{1}H n.m.r. δ 1.47, C3Me, $C4H_3$; 6.33, H1, H2; 7.22, ArH's. Elution with light petroleum-ether(5:1) afforded 4-(4'-chlorophenyl)-2-methyl-3-phenylbut-1-ene(115d)(0.014g) ^{1}H n.m.r. δ 1.60, C2Me; 3.24, Wh/2 27Hz, H3, $C4H_2$; 4.90, Wh/2 6Hz, ClH_2; 7.02, Wh/2 11Hz, ArH's.

Photolysis of trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)

(i) A solution of trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)(0.172g) in anhydrous deoxygenated t-butyl alcohol(150ml) was irradiated(2537Å) as above for 6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)(10%), cis-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(109e)(29%), trans-1-(3'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane (112e)(59%) and 4-(3'-chlorophenyl)-2-methyl-3-phenylbut-1-ene(115e)(2%).

The residue was absorbed onto silver nitrate alumina (13g). Elution with light petroleum-ether(50:1) afforded trans-1-(3'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane (112e)(0.086g) (Found: M^+, 256.1069; C, 79.6; H,6.8. $C_{17}H_{17}Cl$

requires M^+, 256.1017; C, 79.7; H, 6.7%). $\nu_{max}(CCl_4)$ 1020cm^{-1}. λ_{max} 212nm(ε18841), 220(16908),259(1208), 264.5(1208), 272 (1036). ^{1}H n.m.r. δ 0.95, C3Me; 2.35, H1,H2; 7.19, Wh/2 6Hz, ArH's. ^{13}C n.m.r. δ 34.0_2, C1; 34.5_6 C2; 26.1_7, C3; 22.1_6, C3Me; 22.2_5, C3Me; n.o., ClC_1; 129.2_3, ClC_2; 133.9_1, ClC_3; 126.0_3, ClC_4; 129.1_3, ClC_5; 127.1_7, ClC_6; 139.0_9, C2ipso C; 128.9_3, C2ortho C; 128.0_6, C2meta C; 126.0_3, C2para C.

Elution with light petroleum-ether(20:1) gave cis-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(109e)(0.007g) (Found: M^+, 256.0934; C, 79.6; H, 6.7. $C_{17}H_{17}Cl$ requires M^+, 256.1017; C, 79.7; H, 6.7%). $\nu_{max}(CCl_4)$ 690cm^{-1}. ^{1}H n.m.r. δ 1.36, C3Me, $C4H_3$; 5.91, J 13Hz, H2; 6.39, J 13Hz, H1; 7.16, Wh/2 6Hz, ArH's. ^{13}C n.m.r. δ 125.6_9, C1; 142.9_7, C2; 40.9_2, C3; 31.0_6, C3Me, C4; 139.1_0, ClC_1; 126.8_6, ClC_2; 133.9_4, ClC_3; 126.0_8, ClC_4; 129.2_4, ClC_5; 125.6_9, ClC_6; 141.8_8, C3ipso C; 126.2_2, C3ortho C; 128.8_6, C3meta C; 126.0_8, C3para C. Further elution gave trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)(0.015g) ^{1}H n.m.r. δ 1.45, C3Me, $C4H_3$; 6.30, H1, H2; 7.10, Wh/2 12Hz, ArH's.

Elution with light petroleum-ether(5:1) afforded 4-(3'-chlorophenyl)-2-methyl-3-phenylbut-1-ene(115e)(0.004g). $\nu_{max}(CCl_4)$ 895, 1645cm^{-1}. ^{1}H n.m.r. δ 1.60, C2Me; 3.20, Wh/2 20Hz, H3, $C4H_2$; 4.87, Wh/2 7Hz, ClH_2; 7.06, Wh/2 12Hz, ArH's. ^{13}C n.m.r. δ 110.9_9, C1; n.o., C2; 54.3_3, C3; 39.7_9, C4; 21.5_9. C2Me; n.o., C3ipso C; 128.2_7, C3ortho C; 127.9_9, C3meta C; 126.0_6, C3para C; n.o., $C4C_1$; 129.1_0, $C4C_2$; n.o., $C4C_3$; 126.2_1, $C4C_4$; 129.0_0, $C4C_5$; 127.2_0, $C4C_6$.

(ii) A solution of trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)(0.106g) in anhydrous deoxygenated t-butyl alcohol(150ml) was irradiated(2537Å) as above for 0.25hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-

1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)(78%) ^{1}H n.m.r. δ 1.45, C3Me, C4H$_3$; 6.30, H1, H2; 7.10, Wh/2 12Hz, ArH's, cis-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene (109c)(15%) ^{1}H n.m.r. δ 1.36, C3Me, C4H$_3$; 5.91, J 13Hz, H2; 6.39, J 13Hz, H1; 7.16, Wh/2 6Hz, ArH's and trans-1-(3'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112e)(7%) ^{1}H n.m.r. δ 0.95, C3Me; 2.35, H1, H2; 7.19, Wh/2 6Hz, ArH's.

The residue was taken up in anhydrous t-butyl alcohol (150ml), the solution deoxygenated and irradiated for a further 0.25hr. After the removal of the solvent, analysis by ^{1}H n.m.r. showed the presence of trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)(55%), cis-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(109e)(32%) and trans-1-(3'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112e)(13%) by integration of the peaks at δ 1.45, 1.36 and 0.95 respectively.

(iii) A solution of trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)(0.114g) in anhydrous deoxygenated benzene(150ml) was irradiated(2537Å) as above for 6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)(18%), cis-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(109e)(16%), trans-1-(3'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112e) (52%) and 4-(3'-chlorophenyl)-2-methyl-3-phenylbut-1-ene (115e)(14%).

The residue was absorbed onto silver nitrate alumina (13g). Elution with light petroleum-ether(50:1) afforded trans-1-(3'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane (112e)(0.034g) ^{1}H n.m.r. δ 0.95, C3Me; 2.35, H1, H2; 7.19, Wh/2 6Hz, ArH's. Elution with light petroleum-ether(20:1)

gave cis-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(109e) (0.012g) ^{1}H n.m.r. δ 1.36, C3Me, C4H$_3$; 5.91, J 13Hz, H2; 6.39, J 13Hz, H1; 7.16, Wh/2 6Hz, ArH's and trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)(0.016g) ^{1}H n.m.r. δ 1.45, C3Me; C4H$_3$; 6.30, H1, H2; 7.10, Wh/2 12Hz, ArH's. Further elution with light petroleum-ether(5:1) afforded 4-(3'-chlorophenyl)-2-methyl-3-phenylbut-1-ene(115e)(0.006g) ^{1}H n.m.r. δ 1.60, C2Me; 3.20, Wh/2 20Hz, H3, C4H$_2$; 4.87, Wh/2 7Hz, ClH$_2$; 7.06, Wh/2 12Hz, ArH's.

Photolysis of trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(88f)

(i) A solution of trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(88f)(0.107g) in anhydrous deoxygenated t-butyl alcohol(100ml) was irradiated(2537Å) as above for 6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene (88f)(65%), cis-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(109f)(32%) and trans-1-(3',4'-dichlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112f)(3%).

The residue was absorbed onto silver nitrate alumina (13g). Elution with light petroleum-ether(50:1) afforded trans-1-(3',4'-dichlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112f)(0.009g). ^{1}H n.m.r. δ 0.95, C3Me; 2.30, H1, H2; 7.16, ArH's. ^{13}C n.m.r. δ 33.4$_4$, C1; 34.7$_6$, C2; 26.2$_0$, C3; 22.0$_7$, 22.2$_7$, C3Me; 140.2$_3$, Cl$\underline{C}_1$; 130.7$_6$, Cl$\underline{C}_2$, n.o., Cl$\underline{C}_3$, n.o., Cl$\underline{C}_4$; 129.9$_3$, Cl$\underline{C}_5$; 128.6$_6$, Cl$\underline{C}_6$; 139.6$_9$, C2ipso C; 128.8$_7$, C2ortho C; 128.1$_6$, C2meta C; 126.1$_6$, C2para C.

Elution with light petroleum-ether(20:1) gave cis-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(109f) (0.038g). ^{1}H n.m.r. δ 1.39, C3Me, C4H$_3$; 5.95, J 13Hz, H2;

6.43, J 13Hz, H1; 7.16, ArH's. ^{13}C n.m.r. δ 126.3_2, C1; 143.7_9, C2; 40.9_0, C3; 31.0_6, C3Me, C4; 137.6_6, C1C$_1$; 127.8_8, C1C$_2$; n.o., C1C$_3$; n.o., C1C$_4$; 130.3_2, C1C$_5$; 125.7_8, C1C$_6$; 142.3_3, C3ipso C; 126.0_8, C3ortho C; 129.1_9, C3meta C; 125.4_3, C3para C. Further elution afforded trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(88f)(0.033g) ^1H n.m.r. δ 1.45, C3Me, C4H_3; 6.19, J 16Hz, H2; 6.34, J 16Hz, H1; 7.20, ArH's.

(ii) A solution of trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(88f)(0.110g) in anhydrous deoxygenated t-butyl alcohol(150ml) was irradiated(2537Å) as above for 0.25hr. The solvent was removed and the ^1H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene (88f)(56%) ^1H n.m.r. δ 1.45, C3Me, C4H_3; 6.19, J 16Hz, H2; 6.34, J 16Hz, H1; 7.20, ArH's, cis-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(109f)(36%) ^1H n.m.r. δ 1.39, C3Me, C4H_3; 5.95, J 13Hz, H2; 6.43, J 13Hz, H1; 7.16, ArH's and trans-1-(3',4'-dichlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112f)(5%) ^1H n.m.r. δ 0.95, C3Me; 2.30, H1, H2; 7.16, ArH's.

The product was taken up in anhydrous t-butyl alcohol (150ml), the solution deoxygenated and irradiated for a further 0.25hr. After the removal of solvent, analysis of the residue by ^1H n.m.r. showed the presence of trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(88f)(52%), cis-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(109f) (37%) and trans-1-(3',4'-dichlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112f)(11%) by integration of the peaks at δ 1.45, 1.39 and 0.95 respectively.

(iii) A solution of trans-1-(3',4'-dichlorophenyl)-3-

methyl-3-phenylbut-1-ene(88f)(0.101g) in anhydrous deoxygenated benzene(100ml) was irradiated(2537Å) as above for 6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(88f)(53%), cis-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(109f)(39%) and trans-1-(3',4'-dichlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112f)(8%).

The residue was absorbed onto silver nitrate alumina (13g). Elution with light petroleum-ether(50:1) afforded trans-1-(3',4'-dichlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112f)(0.006g) ^{1}H n.m.r. δ 0.95, C3Me; 2.30, H1, H2; 7.16, ArH's. Elution with light petroleum-ether(20:1) gave cis-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(109f)(0.030g) ^{1}H n.m.r. δ 1.39, C3Me, C4H$_3$; 5.95, J 13Hz, H2; 6.43, J 13Hz, H1; 7.16, ArH's and trans-1-(3',4'-dichlorophenyl)-3-methyl-3-phenylbut-1-ene(88f)(0.039g) ^{1}H n.m.r. δ 1.45, C3Me, C4H$_3$; 6.19, J 16Hz, H2; 6.34, J 16Hz, H1; 7.20, ArH's.

Photolysis of trans-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(88g)

(i) A solution of trans-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(88g)(0.113g) in anhydrous deoxygenated t-butyl alcohol(100ml) was irradiated(2537Å) as above for 6hr. The solvent was removed and the ^{1}H n.m.r. of the crude reaction product showed the presence of trans-1-(4'-cyanophenyl)-3,3-dimethyl-2-phenylcyclopropane(112g)(8%) ^{1}H n.m.r. δ 0.98, C3Me; 2.41, H1, H2; 7.20, Wh/2 2Hz, ArH's, trans-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(88g)(6%) ^{1}H n.m.r. δ 1.52, C3Me, C4H$_3$; 6.34, J 16Hz, H2; 6.52, J 16Hz, H1; 7.37, Wh/2 13Hz, ArH's, cis-1-(4'-cyanophenyl)-3-methyl-

3-phenylbut-1-ene(109g)(6%) ^{1}H n.m.r. δ 1.38, C3Me, C4H$_3$; 6.06, J 12Hz, H2; 6.41, J 12Hz, H1; 7.30, ArH's and 4-(4'-cyanophenyl)-2-methyl-3-phenylbut-1-ene(115g)(80%).

The residue was absorbed onto active alumina(13g). Elution with light petroleum-ether(50:1) afforded 4-(4'-cyanophenyl)-2-methyl-3-phenylbut-1-ene(115g)(0.084g). ν_{max}(CCl_4) 890, 1645, 2225cm^{-1}. ^{1}H n.m.r. δ 1.61, C2Me; 3.23, Wh/2 18Hz, H3, C4H$_2$; 4.88, Wh/2 4Hz, ClH$_2$; 7.10, Wh/2 17Hz, ArH's. ^{13}C n.m.r. δ 111.0_6, C1; 146.2_8, C2; 54.0_0, C3; 40.1_3, C4; 21.5_3, C2Me; 118.9_9, ArCN; 141.8_4, C3ipso C; 128.3_1, C3ortho C; 127.8_7, C3meta C; 126.6_0, C3para C; 146.7_3, C4ipso C; 129.7_3, C4ortho C; 131.7_4, C4meta C; 109.6_6, C4para C.

(ii) A solution of trans-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(88g)(0.113g) in anhydrous deoxygenated t-butyl alcohol(100ml) was irradiated(2537Å) as above for 0.25hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(88g)(72%) ^{1}H n.m.r. δ 1.52, C3Me, C4H$_3$; 6.34, J 16Hz, H2; 6.52, J 16Hz, H1; 7.30, ArH's, cis-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(109g)(3%) ^{1}H n.m.r. δ 1.38, C3Me, C4H$_3$; 6.06, J 12Hz, H2; 6.41, J 12Hz, H1; 7.30, ArH's, trans-1-(4'-cyanophenyl)-3,3-dimethyl-2-phenylcyclopropane(112g)(20%) ^{1}H n.m.r. δ 0.98, C3Me; 2.41, H1, H2; 7.20, Wh/2 2Hz, ArH's and 4-(4'-cyanophenyl)-2-methyl-3-phenylbut-1-ene(115g)(5%) ^{1}H n.m.r. δ 1.61, C2Me; 3.23, Wh/2 18Hz, H3, C4H$_2$; 4.88, Wh/2 4Hz, ClH$_2$; 7.10, Wh/2 17Hz, ArH's.

The product was taken up in anhydrous t-butyl alcohol (100ml), the solution deoxygenated and irradiated for a further 0.25hr. After the removal of solvent, analysis of

the residue by ^{1}H n.m.r. showed the presence of trans-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(88g)(40%), cis-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(109g)(6%), trans-1-(4'-cyanophenyl)-3,3-dimethyl-2-phenylcyclopropane (112g)(46%) and 4-(4'-cyanophenyl)-2-methyl-3-phenylbut-1-ene(115g)(8%) by integration of the peaks at δ 1.52, 1.38, 0.98 and 4.88 respectively.

(iii) A solution of trans-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(88g)(0.062g) in anhydrous deoxygenated benzene (100ml) was irradiated(2537Å) as above for 1hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(88g)(43%), cis-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(109g)(5%) ^{1}H n.m.r. δ 1.38, C3Me, $C4H_3$; 6.06, J 12Hz, H2; 6.41, J 12Hz, H1; 7.30, ArH's, trans-1-(4'-cyanophenyl)-3,3-dimethyl-2-phenylcyclopropane(112g)(45%) and 4-(4'-cyanophenyl)-2-methyl-3-phenylbut-1-ene(115g)(7%) ^{1}H n.m.r. δ1.61, C2Me; 3.23, Wh/2 18Hz, H3, $C4H_2$; 4.88, Wh/2 4Hz, $C1H_2$; 7.10, Wh/2 17Hz, ArH's.

The residue was absorbed onto active alumina(13g). Elution with light petroleum-ether(50:1) gave trans-1-(4'-cyanophenyl)-3,3-dimethyl-2-phenylcyclopropane(112g)(0.026g) $\nu_{max}(CCl_4)$ 1025, 2225cm^{-1}. ^{1}H n.m.r. δ 0.98, C3Me; 2.41, H1, H2; 7.20, Wh/2 2Hz, ArH's. ^{13}C n.m.r. δ 34.9_1, C1; 34.5_3, C2; 27.2_0, C3; 22.1_7, C3Me; n.o. ArCN; 145.7_5, C1ipso C; 129.6_7, C1ortho C; 131.8_9, C1meta C; 109.6_7, C1para C; 138.5_6, C2ipso C; 128.9_5, C2ortho C; 128.2_2, C2meta C; 126.3_1, C3para C. Further elution gave trans-1-(4'-cyanophenyl)-3-methyl-3-phenylbut-1-ene(88g)(0.028g) ^{1}H n.m.r. δ 1.52, C3Me, $C4H_3$; 6.34, J 16Hz, H2; 6.52, J 16Hz, H1; 7.37, Wh/2 13Hz, ArH's.

1,3-Diphenyl-3-methylbutan-1-one(92a)

Jones reagent was added dropwise to a solution of 1,3-diphenyl-3-methylbutan-1-ol(97a)(2.5g) in acetone(70ml) until an orange/brown colour persisted[118]. The resulting mixture was stirred for 0.5hr before sodium bisulphite was added. The solution was decanted and the residue washed with light petroleum. The combined organic fractions were washed with saturated sodium bicarbonate and sodium chloride solutions and dried over magnesium sulphate. The oil isolated on removal of the solvent was 1,3-diphenyl-3-methylbutan-1-one(92a)(2.5g)(Found: M^+, 238.1276; C, 85.6; H, 7.4. $C_{17}H_{18}O$ requires M^+, 238.1357; C, 85.6; H, 7.6%). ν_{max}(neat) 1675,1690cm^{-1}. λ_{max} 211nm(ε6058), 238(7885), 278.5(769), 287.5(577). ^1H n.m.r. δ 1.50, C3Me, $C4H_3$; 3.27, $C2H_2$; 7.50, Wh/2 43Hz, ArH's. ^{13}C n.m.r. δ 199.0_4, C1; 50.8_8, C2; 37.5_2, C3; 29.1_1, C3Me, C4; 138.2_1, C1ipso C; 128.3_8, C1ortho C; 128.0_7, C1meta C; 132.6_5, C1para C; 148.8_8, C3ipso C; 125.4_6, C3ortho C; 128.1_7, C3meta C; 125.7_8, C3para C.

1-d-1,3-diphenyl-3-methylbutan-1-ol(133a)

1,3-Diphenyl-3-methylbutan-1-one(92a)(2.6g) was taken up in dry ether and added to a stirred suspension of lithium aluminium deuteride(0.3g) in dry ether[119]. The mixture was heated under reflux for 5hr, quenched by dropwise addition of water and stirred with 10% sulphuric acid(20ml). The aqueous layer was extracted with ether and the combined ethereal fractions were washed with aqueous sodium bicarbonate. The product isolated on the removal of solvent was 1-d-1,3-diphenyl-3-methylbutan-1-ol(133a)(2.6g, m.p. 90-91°C)(Found: M^+, 241.1519. $C_{17}H_{19}DO$ requires M^+, 241.1572). ν_{max}(neat) 3425cm^{-1}. ^1H n.m.r. δ 1.28, C3Me, OH; 1.40, $C4H_3$; 1.89, J 15Hz, H2; 2.01, J 15Hz, H2'; 7.05, Wh/2 2Hz, C3ArH's;

7.22, Wh/2 4Hz, ClArH's. ^{13}C n.m.r. δ 53.6_1, C2; 37.4_4, C3; 29.4_9, C3Me, C4; 145.8_4, Clipso C; 125.5_4, Clortho C; 128.2_2, Clmeta C; 127.0_3, Clpara C; 148.7_3, C3ipso C; 125.8_9, C3ortho C; 128.2_2, C3meta C; 125.7_3, C3para C.

trans-1-d-1,3-Diphenyl-3-methylbut-1-ene(110a)

p-Toluenesulphonic acid(0.4g) was added to a solution of 1-d-1,3-diphenyl-3-methylbutan-1-ol(133a)(2.4g) in benzene and the mixture was heated under reflux for 0.5hr with azeotropic removal of water[58]. The reaction mixture was cooled, washed with water, sodium carbonate solution, water and sodium chloride solution, and dried over anhydrous magnesium sulphate. The product isolated after the removal of solvent was trans-1-d-1,3-diphenyl-3-methylbut-1-ene(110a) (2.0g) (Found: M^+, 223.1485. $C_{17}H_{17}D$ requires M^+, 223.1470). ν_{max}(neat) 910cm^{-1}. ^{1}H n.m.r. δ 1.50, C3Me, $C4H_3$; 6.40, Wh/2 6Hz, H2; 7.26, Wh/2 5Hz, ArH's. ^{13}C n.m.r. δ 139.9_7, C2; 40.7_0, C3; 28.7_1, C3Me, C4; 137.6_2, Clipso C; 126.1_5, Clortho C; 128.4_4, Clmeta C; 126.9_6, Clpara C; 148.6_6, C3ipso C; 126.1_5, C3ortho C; 128.1_5, C3meta C; 125.8_6, C3para C.

1-(4'-Methoxyphenyl)-3-methyl-3-phenylbutan-1-one(92b)

Jones reagent was added to a solution of 1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-1-ol(97b)(0.9g) in acetone until an orange/brown colour persisted. The residue, isolated as above, was 1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-1-one(92b)(0.7g) (Found: M^+, 268.1462; C, 80.6; H, 7.5. $C_{18}H_{20}O_2$ requires M^+, 268.1309; C, 80.6; H, 7.5%). ν_{max}(neat) 1660, 1680cm^{-1}. λ_{max} 209.5nm(ε19134), 266.5 (17388). ^{1}H n.m.r. δ 1.48, C3Me, $C4H_3$; 3.20, $C2H_2$; 3.78, ArOMe; 7.25, Wh/2 69Hz, ArH's. ^{13}C n.m.r. δ 197.4_8, C1;

50.4_6, C2; 37.5_8, C3; 29.0_9, C3Me, C4; 55.3_3, ArOMe; 131.3_2, Clipso C; 130.3_4, Clortho C; 113.5_0, Clmeta C; n.o., Clpara C; 149.0_8, C3ipso C; 125.4_1, C3ortho C; 128.1_5, C3meta C; 125.7_1, C3para C.

1-d-1-(4'-Methoxyphenyl)-3-methyl-3-phenylbutan-1-ol(133b)

A solution of 1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-1-one(92b)(0.6g) in dry ether was added to a stirred suspension of lithium aluminium deuteride(0.07g) in dry ether and the resulting mixture was heated under reflux for 0.5hr. The oil, isolated as above, was 1-d-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-1-ol(133b)(0.58g) (Found: M^+, 253.1581. $C_{18}H_{21}DO_2$ requires M^+, 271.1681; M^+-H_2O, 253.1576). ν_{max}(neat) 3450cm^{-1}. ^{1}H n.m.r. δ 1.32, C3Me; 1.40, $C4H_3$, OH; 1.92, J 15Hz, H2; 2.14, J 15Hz, H2'; 7.10, Wh/2 29Hz, ArH,s. ^{13}C n.m.r. δ 53.6_2, C2; 37.4_4, C3; 29.2_8, C3Me; 29.9_0, C4; 55.2_1, ArOMe; n.o., Clipso C; 126.8_5, Clortho C; 113.7_6, Clmeta C; 158.7_8, Clpara C; 148.7_9, C3ipso C; 125.9_8, C3ortho C; 128.3_1, C3meta C; 125.8_2, C3para C.

trans-1-d-1-(4'-Methoxyphenyl)-3-methyl-3-phenylbut-1-ene(110b)

p-Toluenesulphonic acid(0.1g) was added to a solution of 1-d-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-1-ol(133b) (0.49g) in benzene and the resulting mixture was heated under reflux for 0.25hr. The oil, isolated as above, was trans-1-d-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene (110b)(0.33g) (Found: M^+, 253.1541. $C_{18}H_{19}DO$ requires 253.1576). ν_{max}(neat) 900, 1230cm^{-1}. ^{1}H n.m.r. δ 1.45, C3Me, $C4H_3$; 3.62, ArOMe; 6.22, Wh/2 5Hz, H2; 7.00, Wh/2 32Hz, ArH's. ^{13}C n.m.r. δ 138.0_0, C2; 40.6_4, C3; 28.8_2, C3Me, C4; 55.1_9, ArOMe; 130.4_3, Clipso C; 127.2_1, Clortho C;

113.8$_4$, Clmeta C; 158.8$_0$, Clpara C; 148.9$_4$, C3ipso C; 126.1$_9$, C3ortho C; 128.1$_4$, C3meta C; 125.8$_0$, C3para C.

1-(4'-Methylphenyl)-3-methyl-3-phenylbutan-1-one(92c)

Jones reagent was added dropwise to a solution of 1-(4'-methylphenyl)-3-methyl-3-phenylbutan-1-ol(97c)(1.0g) in acetone until an orange/brown colour persisted. The oil, isolated as above, was 1-(4'-methylphenyl)-3-methyl-3-phenylbutan-1-one(92c)(0.87g) (Found: M^+, 252.1513. $C_{18}H_{20}O$ requires M^+, 252.1513). $\nu_{max}(CCl_4)$ 1670, 1690cm^{-1}. λ_{max} 210.5nm(17117), 248.5(14929), 287(6435). ^{1}H n.m.r. δ 1.49, C3Me, C4H$_3$; 2.33, ArMe; 3.25, C2H$_2$; 7.39, Wh/2 45Hz, ArH's. ^{13}C n.m.r. δ 198.2$_9$, C1; 50.6$_4$, C2; 37.5$_5$, C3; 29.2$_5$, C3Me, C4; 21.6$_1$, ArMe; 143.3$_1$, Clipso C; 128.3$_2$, Clortho C; 129.2$_3$, Clmeta C; 135.8$_7$, Clpara C; 149.2$_4$, C3ipso C; 125.5$_9$, C3ortho C; 128.3$_2$, C3meta C; 125.8$_5$, C3para C.

1-d-1-(4'-Methylphenyl)-3-methyl-3-phenylbutan-1-ol(133c)

A solution of 1-(4'-methylphenyl)-3-methyl-3-phenylbutan-1-one(92c)(0.5g) in dry ether was added to a stirred suspension of lithium aluminium deuteride(0.05g) in dry ether and the resulting mixture was heated under reflux for 6hr. The oil, isolated as above, was 1-d-1-(4'-methylphenyl)-3-methyl-3-phenylbutan-1-ol(133c)(0.5g) (Found: M^+, 237.1635. $C_{18}H_{21}DO$ requires M^+, 255.1732; M^+-H_2O, 237.1627). $\nu_{max}(CCl_4)$3640cm^{-1}. ^{1}H n.m.r. δ 1.25, C3Me; 1.38, C4H$_3$; 1.84, J 14Hz, H2; 1.96, J 14Hz, H2'; 2.20, OH; 2.43, ArMe; 6.89, C3ArH's; 7.38, ClArH's. ^{13}C n.m.r. δ 53.6$_6$, C2; 37.4$_9$, C3; 29.3$_3$, C3Me; 29.6$_7$, C4; 21.0$_3$, ArMe; 142.9$_3$, Clipso C; 125.5$_6$, Clortho C; 129.0$_0$, Clmeta C; 136.6$_6$, Clpara C; 148.8$_1$, C3ipso C; 125.9$_6$, C3ortho C; 128.2$_8$, C3meta C; 125.7$_8$, C3para C.

trans-1-d-1-(4'-Methylphenyl)-3-methyl-3-phenylbut-1-ene(110c)

p-Toluenesulphonic acid was added to a solution of 1-d-1-(4'-methylphenyl)-3-methyl-3-phenylbutan-1-ol(133c) (0.5g) in benzene and the resulting mixture was heated under reflux for 0.25hr. The oil, isolated as above, was trans-1-d-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene (110c)(0.44g) (Found: M^+, 237.1603. $C_{18}H_{19}D$ requires M^+, 237.1627). $\nu_{max}(CCl_4)$ 975cm^{-1}. ^{1}H n.m.r. δ 1.53, C3Me, C4H$_3$; 2.33, ArMe; 6.37, Wh/2 6Hz, H2; 7.25, Wh/2 15Hz, ArH's. ^{13}C n.m.r. δ 139.0$_6$, C2; 40.6$_8$, C3; 28.7$_7$, C3Me, C4; 21.0$_9$, ArMe; 134.8$_5$, C1ipso C; 126.0$_4$, C1ortho C; 129.1$_9$, C1meta C; 136.6$_6$, C1para C; 148.8$_7$, C3ipso C; 126.2$_2$, C3ortho C; 128.1$_2$, C3meta C; 125.8$_2$, C3para C.

1-d-3,3-Dimethyl-1-(4'-methylphenyl)indane(111c)

p-Toluenesulphonic acid(0.1g) was added to a solution of 1-d-1-(4'-methylphenyl)-3-methyl-3-phenylbutan-1-ol(133c) (0.4g) in benzene and the resulting mixture was heated under reflux for 0.5hr. The oily residue, isolated as above, was absorbed onto silver nitrate alumina(50g). Elution with light petroleum-ether(50:1) afforded 1-d-3,3-dimethyl-1-(4'-methylphenyl)indane(111c)(0.22g, m.p. 68-70^{0}C) (Found: M^+, 237.1618. $C_{18}H_{19}D$ requires M^+, 237.1627). ^{1}H n.m.r. δ 1.24, 1.40, C3Me; 2.31, ArMe; 1.94, J 12Hz, H2; 2.36, J 12Hz, H2'; 7.06, Wh/2 5Hz, ArH's. ^{13}C n.m.r. δ 21.0$_0$, ArMe; 28.6$_8$, 29.0$_7$, C3Me; 43.0$_4$, C3; 52.7$_0$, C2; 121.7$_9$, 124.9$_2$, 126.4$_8$, 126.8$_2$, C5, C6, C7, C8; 128.2$_4$, C1ortho C; 129.1$_2$, C1meta C; 135.6$_6$, C1para C; 142.0$_7$, C1ipso C; 145.4$_8$, C4; 152.7$_0$, C9. Further elution with light petroleum-ether(20:1) afforded trans-1-d-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(110c)(0.058g) ^{1}H n.m.r. δ 1.53, C3Me, C4H$_3$; 2.33, ArMe; 6.37, Wh/2 6Hz, H2; 7.25, Wh/2 15Hz, ArH's.

1-(4'-Chlorophenyl)-3-methyl-3-phenylbutan-1-one(92d)

Jones reagent was added dropwise to a solution of 1-(4'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(97d)(1.5g) in acetone until an orange/brown colour persisted. The oily residue, isolated as above, was 1-(4'-chlorophenyl)-3-methyl-3-phenylbutan-1-one(92d)(1.5g) (Found: M^+, 272.0883; C, 75.3; H, 6.4. $C_{17}H_{17}ClO$ requires M^+, 272.0966; C, 75.0; H, 6.3%). ν_{max}(neat) 1675, 1690cm^{-1}. λ_{max} 210nm(11387), 251.5(16204. ^{1}H n.m.r. δ 1.47, C3Me, C4H_3; 3.21, C2H_2; 7.39, Wh/2 26Hz, ArH's. ^{13}C n.m.r. δ 197.5$_1$, C1; 50.9$_5$, C2; 37.5$_3$, C3; 29.0$_5$, C3Me, C4; 136.4$_6$, C1ipso C; 129.4$_4$, C1ortho C; 128.6$_0$, C1meta C; 138.8$_1$, C1para C; 148.5$_4$, C3ipso C; 125.4$_2$, C3ortho C; 128.1$_7$, C3meta C; 125.8$_4$, C3para C.

1-d-1-(4'-Chlorophenyl)-3-methyl-3-phenylbutan-1-ol(133d)

A solution of 1-(4'-chlorophenyl)-3-methyl-3-phenylbutan-1-one(92d)(1.4g) in dry ether was added to a stirred suspension of lithium aluminium deuteride(0.15g) in dry ether and the resulting mixture was heated under reflux for 5hr. The residue, isolated as above, crystallised on removal of solvent. Recrystallisation from a light petroleum-ether mixture gave 1-d-1-(4'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(133d)(1.4g, m.p. 88-89^{0}C) (Found: M^+, 275.1238. $C_{17}H_{18}ClDO$ requires M^+, 275.1186). ν_{max}(neat) 3420cm^{-1}. ^{1}H n.m.r. δ 1.28, C3Me; 1.35, C4H_3; 1.80, OH; 1.90, J 16Hz, H2; 2.05, J 16Hz, H2'; 7.15, Wh/2 16Hz, ArH's. ^{13}C n.m.r. δ 53.6$_6$, C2; 37.3$_4$, C3; 29.2$_4$, C3Me; 29.6$_3$, C4; 144.1$_2$, C1ipso C; 125.8$_7$, C1ortho C; 128.3$_1$, C1meta C; 132.6$_0$, C1para C; 148.3$_0$, C3ipso C; 127.8$_7$, C3ortho C; 128.3$_1$, C3meta C; 126.9$_4$, C3para C.

trans-1-d-1-(4'-Chlorophenyl)-3-methyl-3-phenylbut-1-ene(110d)

p-Toluenesulphonic acid(0.2g) was added to a solution of 1-d-1-(4'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(133d) (1.25g) in benzene and the resulting mixture was heated under reflux for 0.5hr. The oil, isolated as above, was trans-1-d-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene (110d)(0.75g) (Found: M^+, 257.1051. $C_{17}H_{16}ClD$ requires M^+, 257.1081). ν_{max}(neat) 900cm^{-1}. ^1H n.m.r. δ 1.45, C3Me, $C4H_3$; 6.40, Wh/2 5Hz, H2; 7.30, Wh/2 7Hz, ArH's. ^{13}C n.m.r. δ 140.7_3, C2; 40.7_3, C3; 28.6_1, C3Me, C4; 136.0_7, Clipso C; 127.3_2, Clortho C; 128.5_6, Clmeta C; 132.5_1, Clpara C; 148.3_3, C3ipso C; 126.1_2, C3ortho C; 128.1_7, C3meta C; 125.9_4, C3para C.

1-(3'-Chlorophenyl)-3-methyl-3-phenylbutan-1-one(92e)

Jones reagent was added dropwise to a solution of 1-(3'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(97e)(0.9g) in acetone until an orange/brown colour persisted. The oil, isolated as above, was 1-(3'-chlorophenyl)-3-methyl-3-phenylbutan-1-one(92e)(0.9g). ν_{max}(neat) 1674, 1692cm^{-1}. λ_{max} 215nm (ε15000), 239(8735), 283(1024), 290(1084), 299(663). ^1H n.m.r. δ 1.45, C3Me, $C4H_3$; 3.17, $C2H_2$; 7.35, Wh/2 12Hz, ArH's. ^{13}C n.m.r. δ 197.6_3, C1; 51.1_7, C2; 37.6_2, C3; 29.0_7, C3Me, C4; 139.7_0, $C1C_1$; 128.2_1, $C1C_2$; 134.6_6, $C1C_3$; 132.4_8, $C1C_4$; 129.6_6, $C1C_5$; 126.1_1, $C1C_6$; 148.4_1, C3ipso C; 125.4_4, C3ortho C; 128.2_1, C3meta C; 125.9_4, C3para C.

1-d-1-(3'-Chlorophenyl)-3-methyl-3-phenylbutan-1-ol(133e)

A solution of 1-(3'-chlorophenyl)-3-methyl-3-phenylbutan-1-one(92e)(0.8g) in dry ether was added to a stirred suspension of lithium aluminium deuteride in dry ether and the resulting mixture was heated under reflux for 5hr. The

oil, isolated as above, was 1-d-1-(3'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(133e)(0.79g) (Found: M^+, 275.0178. $C_{17}H_{18}ClDO$ requires M^+, 275.1186). ν_{max}(neat) 3420cm^{-1}. ^1H n.m.r. δ 1.32, C3Me; 1.39, $C4H_3$; 1.62, OH; 1.86, J 14Hz, H2; 2.10, J 14Hz, H2'; 7.10, Wh/2 14Hz, ArH's. ^{13}C n.m.r. δ 53.7_2, C2; 37.4_4, C3; 29.3_0, C3Me; 29.6_3, C4; 147.8_0, ClC_1; 125.8_7, ClC_2; 134.1_2, ClC_3; 127.1_6, ClC_4; 129.5_3, ClC_5; 123.6_7, ClC_6; 148.2_9, C3ipso C; 125.9_6, C3ortho C; 128.3_6, C3meta C; 125.8_7, C3para C.

trans-1-d-1-(3'-Chlorophenyl)-3-methyl-3-phenylbut-1-ene(110e)

p-Toluenesulphonic acid was added to a solution of 1-d-1-(3'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(133e) (0.69g) in benzene and the resulting mixture was heated under reflux for 0.5hr. The oil, isolated as above, was trans-1-d-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene (110e)(0.56g) (Found: M^+, 257.1017. $C_{17}H_{16}ClD$ requires M^+, 257.1081). ν_{max}(neat) 910cm^{-1}. ^1H n.m.r. δ 1.47, C3Me, $C4H_3$; 6.33, Wh/2 5Hz, H2; 7.15, Wh/2 12Hz ArH's. ^{13}C n.m.r. δ 141.6_0, C2; 40.7_6, C3; 28.5_8, C3Me, C4; 139.6_1, ClC_1; 126.8_7, ClC_2; 134.3_6, ClC_3; 126.8_7, ClC_4; 129.6_5, ClC_5; 124.3_8, ClC_6; 148.2_1, C3ipso C; 126.1_2, C3ortho C; 128.2_4, C3meta C; 126.0_1, C3para C.

Photolysis of trans-1-d-1,3-diphenyl-3-methylbut-1-ene(110a)

A solution of trans-1-d-1,3-diphenyl-3-methylbut-1-ene (110a)(0.110g) in deoxygenated anhydrous benzene(150ml) was irradiated(2537Å) for 6hr in a quartz vessel under a nitrogen atmosphere. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-d-1,3-diphenyl-3-methylbut-1-ene(110a)(3%) ^{1}H n.m.r. δ 1.50, C3Me, $C4H_3$; 6.40, H2; 7.26, ArH's, cis-1-d-1,3-diphenyl-3-methylbut-1-ene(137a)(3%) ^{1}H n.m.r. δ 1.32, C3Me, $C4H_3$; 6.10, H2; 7.15, ArH's, trans-1-d-3,3-dimethyl-1,2-diphenylcyclopropane(134a)(44%) and a 1:1 mixture of 3-d- and 4-d-3,4-diphenyl-2-methylbut-1-ene (135a,136a).

The residue was absorbed onto silver nitrate alumina (13g). Elution with light petroleum-ether(50:1) afforded trans-1-d-3,3-dimethyl-1,2-diphenylcyclopropane(134a)(0.046g) (Found: M^+, 223.1409. $C_{17}H_{17}D$ requires M^+, 223.1470). ^{1}H n.m.r. δ 0.93, C3Me; 2.30, H2; 7.12, ArH's. ^{13}C n.m.r. δ 34.2_2, C2; 25.6_5, C3; 22.2_2, C3Me; 139.5_3, C1-, C2ipso C; 128.9_9, C1-, C2ortho C; 127.9_8, C1-, C2meta C; 125.8_3, C1-, C2para C. Further elution with light petroleum-ether(10:1) gave 3-d- and 4-d-3,4-diphenyl-2-methylbut-1-ene(135a, 136a) (0.047g). $\nu_{max}(CCl_4)$ 890, 1645cm^{-1}. ^{1}H n.m.r. δ 1.59, C2Me; 3.19, Wh/2 25Hz, H3, $C4H_2$, C4HD; 4.82, Wh/2 9Hz $C1H_2$; 7.00, Wh/2 9Hz, ArH's. ^{13}C n.m.r. δ 110.8_5, C1; 147.3_6, C2; 54.4_0, C3; 39.8_5, C4; 21.5_0, C2Me; 142.8_7, C3ipso C; 128.1_3, C3ortho C; 128.0_0, C3meta C; 126.2_3, C3para C; 140.5_7, C4ipso C; 128.9_6, C4ortho C; 128.0_0, C4meta C; 125.7_4, C4para C.

Photolysis of trans-1-d-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(110c)

A solution of trans-1-d-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(110c)(0.150g) in anhydrous deoxygenated benzene(150ml) was irradiated(2537Å) as above for 6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-d-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(110c)(4%) ^{1}H n.m.r. δ 1.53, C3Me, $C4H_3$; 2.33, ArMe; 6.37, Wh/2 6Hz, H2; 7.25, Wh/2 15Hz, ArH's, cis-1-d-1-(4'-methylphenyl)-3-methyl-3-phenylbut-1-ene(137c)(4%) ^{1}H n.m.r. δ 1.33, C3Me, $C4H_3$; 2.25, ArMe; 5.83, Wh/2 5Hz, H2; 7.20, ArH's, trans-1-d-3,3-dimethyl-1-(4'-methylphenyl)-2-phenylcyclopropane(134c)(77%) and 4-d-4-(4'-methylphenyl)-2-methyl-3-phenylbut-1-ene(135c)(15%).

The residue was absorbed onto silver nitrate alumina (13g). Elution with light petroleum-ether(50:1) gave trans-1-d-3,3-dimethyl-1-(4'-methylphenyl)-2-phenylcyclopropane (134c)(0.097g) $\nu_{max}(CCl_4)$ 1025cm^{-1}. ^{1}H n.m.r. δ 0.97, C3Me; 2.30, ArMe, H2; 7.05, C2ArH's; 7.19, ClArH's. ^{13}C n.m.r. δ 34.2_9, C2; 25.5_5, C3; 22.2_6, C3Me; 21.0_0, ArMe; 136.4_3, Clipso C; 128.9_1, Clortho C; 128.7_6, Clmeta C; 135.2_6, Clpara C; 139.7_9, C2ipso C; 129.0_6, C2ortho C; 127.9_9, C2meta C; 125.7_9, C2para C. Further elution with light petroleum-ether(5:1) afforded 4-d-4-(4'-methylphenyl)-2-methyl-3-phenylbut-1-ene(135c)(0.019g). $\nu_{max}(CCl_4)$ 890, 1640cm^{-1}. ^{1}H n.m.r. δ 1.59,C2Me; 2.26, ArMe; 3.16, Wh/2 30Hz, H3, H4; 4.86, Wh/2 9Hz, ClH_2; 7.05, C4ArH's; 7.16, C3ArH's. ^{13}C n.m.r. δ 110.8_5, C1; 147.5_2, C2; 54.4_7, C3; 21.5_0, C2Me; 21.0_1, ArMe; 143.0_8, C3ipso C; 128.1_4, C3ortho C; 128.0_4, C3meta C; 126.2_2, C3para C; n.o., C4ipso C; 128.9_6, C4ortho C; 128.7_6, C4meta C; 135.3_1, C4para C.

Photolysis of trans-1-d-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(110d)

A solution of trans-1-d-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(110d)(0.135g) in anhydrous deoxygenated benzene(150ml) was irradiated(2537Å) as above for 6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of trans-1-d-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(110d)(17%), cis-1-d-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(137d)(22%), trans-1-d-3,3-dimethyl-1-(4'-chlorophenyl)-2-phenylcyclopropane(134d)(41%) and 4-d-4-(4'-chlorophenyl)-2-methyl-3-phenylbut-1-ene(135d)(20%).

The residue was absorbed onto silver nitrate alumina (13g). Elution with light petroleum-ether(50:1) afforded trans-1-d-1-(4'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(134d)(0.055g) (Found: M^{+}, 257.1088. $C_{17}H_{16}ClD$ requires M^{+}, 257.1081). $\nu_{max}(CCl_4)$ 1010cm^{-1}. ^{1}H n.m.r. δ 0.95, C3Me; 2,32, H2; 7.22, Wh/2 4Hz, ArH's. ^{13}C n.m.r. δ 34.5_5, C2; 25.9_1, C3; 22.1_2, C3Me; 22.2_6, C3Me; 138.1_7, Clipso C; 130.3_6, Clortho C; 128.1_4, Clmeta C; 131.6_7, Clpara C; 139.2_6, C2ipso C; 129.0_0, C2ortho C; 128.1_4, C2meta C; 126.0_2, C2para C. Elution with light petroleum-ether(10:1) gave cis-1-d-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(137d)(0.028g) ^{1}H n.m.r. δ 1.35, C3Me, $C4H_3$; 5.90, Wh/2 5Hz, H2; 7.20, Wh/2 4Hz, ArH's and trans-1-d-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(110d)(0.018g) ^{1}H n.m.r. δ 1.45, C3Me, $C4H_3$; 6.40, Wh/2 5Hz, H2; 7.30, Wh/2 7Hz, ArH's. Further elution with light petroleum-ether (5:1) afforded 4-d-4-(4'-chlorophenyl)-2-methyl-3-phenylbut-1-ene(135d)(0.016) (Found: M^{+}, 257.1094. $C_{17}H_{16}ClD$ requires M^{+}, 257.1081). $\nu_{max}(CCl_4)$ 890, 1640cm^{-1}. ^{1}H n.m.r. δ 1.55, C2Me; 3.08, J 6Hz, H4; 3.35, J 6Hz, H3; 4.82, Wh/2

6Hz, ClH_2; 7.00, Wh/2 12Hz, ArH's. ^{13}C n.m.r. δ 110.9_1, Cl; n.o., C2; 54.4_0, C3; 21.5_9, C2Me; n.o., C3ipso C; 128.1_2, C3ortho C; 127.9_8, C3meta C; 126.4_2, C3para C; n.o., C4ipso C; 130.2_9, C4ortho C; 128.2_3, C4meta C; n.o., C4para C.

Photolysis of trans-1-d-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(110e)

A solution of trans-1-d-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(110e)(0.130g) in anhydrous deoxygenated benzene(100ml) was irradiated as above for 6hr. The solvent was removed and the spectrum of the crude reaction product showed the presence of trans-1-d-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(110e)(19%), cis-1-d-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(137e)(22%), trans-1-d-1-(3'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(134e)(44%) and 4-d-4-(3'-chlorophenyl)-2-methyl-3-phenylbut-1-ene(135e)(14%).

The residue was absorbed onto silver nitrate alumina (13g). Elution with light petroleum-ether(50:1) afforded trans-1-d-1-(3'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(134e)(0.031g) ^1H n.m.r. δ 0.96, C3Me; 2.33, H2; 7.20, Wh/2 6Hz, ArH's. ^{13}C n.m.r. δ 34.4_7, C2; 26.1_3, C3; 22.1_2, C3Me; 22.2_5, C3Me; 141.8_4, ClC_1; 129.2_5, ClC_2; 133.9_3, ClC_3; 126.0_9, ClC_4; 129.1_5, ClC_5; 127.2_0, ClC_6; 139.0_9, C2ipso C; 128.9_8, C2ortho C; 128.1_2, C2meta C; 126.0_9, C2para C. Elution with light petroleum-ether(20:1) gave cis-1-d-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(137e)(0.014g) ^1H n.m.r. δ 1.36, C3Me, $C4H_3$; 5.93, Wh/2 8Hz, H2; 7.20, Wh/2 4Hz, ArH's and trans-1-d-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(110e)(0.009g) ^1H n.m.r. δ 1.47, C3Me, $C4H_3$; 6.35, Wh/2 5Hz H2; 7.15, Wh/2 12Hz, ArH's. Further elution with light petroleum-ether(5:1) afforded

4-d-4-(3'-chlorophenyl)-2-methyl-3-phenylbut-1-ene(135e) (0.021g) ^{1}H n.m.r. δ 1.60, C2Me; 3.23, Wh/2 32Hz, H3, H4; 4.86, Wh/2 6Hz, ClH_2; 7.21, Wh/2 4Hz, ArH's. ^{13}C n.m.r. δ 111.0_0, C1; n.o., C2; 54.1_6, C3; 22.2_8, C2Me; 141.8_1, C3ipso C; 128.1_9, C3ortho C; 128.0_7, C3meta C; 126.2_3, C3para C; 140.4_4, $C4C_1$; 129.1_5, $C4C_2$; n.o., $C4C_3$; 126.4_3, $C4C_4$; 129.0_6, $C4C_5$; 127.0_8, $C4C_6$.

Photolysis of trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a)

(i) A solution of trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a)(1.01g) in anhydrous deoxygenated light petroleum(200ml), in a quartz vessel under a nitrogen atmosphere, was irradiated(2537Å) for 8hr and the reaction was monitored by g.l.c. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of 1,3-diphenyl-3-methylbutan-2-one(139a) δ_H 3.48, ClH_2, 2,3-diphenyl-3-methylbutanal(140a) δ_H 3.72, J 3Hz, H2; 9.79, J 3Hz, H1, 1,2-diphenyl-2-methylpropane(142a) δ_H 2.85, ClH_2, 1,2-diphenylethane(143a) δ_H 2.90, ClH_2, $C2H_2$ and unreacted trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a) δ_H 3.02, J 2Hz, H2; 3.73, J 2Hz, H1.

The residue was absorbed onto alumina(80g). Elution with light petroleum gave 2,3-dimethyl-2,3-diphenylbutane (141)(0.108g) (Found: M^+, 238.1720. $C_{18}H_{22}$ requires M^+, 238.1735). ^{1}H n.m.r. δ 1.28, Me; 7.08, ArH's. ^{13}C n.m.r. δ 25.1_9, C1, C2Me, C3Me, C4; 43.6_5, C2, C3; 146.8_2, C2-, C3ipso C; 126.6_0, C2-, C3ortho C; 128.6_1, C2-, C3meta C; 125.4_8, C2-, C3para C. Further elution gave 1,2-diphenyl-2-methylpropane(142a)(0.116g) (Found: M^+, 210.1408. $C_{16}H_{18}$ requires M^+, 210.1409). ^{1}H n.m.r. δ 1.30, C2Me, $C3H_3$; 2.85, ClH_2; 7.15, ArH's. ^{13}C n.m.r. δ 51.1_6, C1; 38.8_0, C2; 28.2_1, C2Me, C3; 138.8_8, C1ipso C; 130.4_2, C1ortho C; 127.4_3, C1meta C; 125.8_7, C1para C; 149.0_1, C2ipso C; 126.2_1, C2ortho C; 127.9_2, C2meta C; 125.6_5, C2para C. Further elution afforded 1,2-diphenylethane(143a)(0.064g) (Found: M^+, 182.1132. $C_{14}H_{14}$ requires M^+, 182.1095). ^{1}H n.m.r. δ 2.90, ClH_2, $C2H_2$; 7.12, ArH's. ^{13}C n.m.r. δ 37.9_4, C1, C2; 141.7_5, C1-, C2ipso C; 128.4_6, C1-, C2ortho C; 128.3_1, C1-, C2meta C; 125.9_2, C1-, C2para C.

Elution with light petroleum-ether(20:1) afforded

trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a)(0.107g) ^{1}H n.m.r. δ 1.32, C3Me; 1.41, $C4H_3$; 3.02, J 2Hz, H2; 3.73, J 2Hz, H1; 7.32, ArH's and 1,3-diphenyl-3-methylbutan-2-one (139a)(0.068g) (Found: M^+, 238.1357; C, 85.3; H, 7.4. $C_{17}H_{18}O$ requires M^+, 238.1358; C, 85.7; H, 7.6%). $\nu_{max}(CHCl_3)$ 1715cm^{-1}. λ_{max} 212.5nm(ε7143), 253.5(417), 259(437), 265 (377). ^{1}H n.m.r. δ 1.50, C3Me, $C4H_3$; 3.48, $C1H_2$; 7.10, ArH's. ^{13}C n.m.r. δ 44.1_2, C1; 209.8_1, C2; 52.8_2, C3; 25.0_8, C3Me, C4; 135.0_8, C1ipso C; 129.4_8, C1ortho C; 128.2_7, C1meta C; 126.5_6, C1para C; 143.6_7, C3ipso C; 126.3_4, C3ortho C; 128.9_1, C3meta C; 127.1_0, C3para C.

(ii) A solution of trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a)(0.573g) in anhydrous deoxygenated benzene (150ml) was irradiated as above for 6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of 1,3-diphenyl-3-methylbutan-2-one(139a) δ_H 3.48, $C1H_2$, 2,3-diphenyl-3-methylbutanal(140a) δ_H 3.72, J 3Hz, H2; 9.79, J 3Hz, H1, 1,2-diphenyl-2-methyl-propane(143a) δ_H 2.90, $C1H_2$, $C2H_2$ and unreacted trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a) δ_H 3.02, J 2Hz, H2; 3.73, J 2Hz, H1.

The residue was absorbed onto alumina(80g). Elution with light petroleum gave 2,3-dimethyl-2,3-diphenylbutane (141)(0.051g) ^{1}H n.m.r. δ 1.28, $C1H_3$, C2Me, C3Me, $C4H_3$; 7.08 ArH's, 1,2-diphenyl-2-methylpropane(142a)(0.062g) ^{1}H n.m.r. δ 1.30, C2Me, $C3H_3$; 2.85, $C1H_2$; 7.15, ArH's and 1,2-diphenylethane(143a)(0.050g) ^{1}H n.m.r. δ 2.90, $C1H_2$, $C2H_2$; 7.12, ArH's. Further elution with light petroleum-ether(20:1) afforded trans-1,3-diphenyl-1,2-epoxy-3-methyl-butane(89a)(0.157g) ^{1}H n.m.r. δ 1.32, C3Me; 1.41, $C4H_3$; 3.02, J 2Hz, H2; 3.73, J 2Hz, H1; 7.32, ArH's and 1,3-diphenyl-3-methylbutan-2-one(139a)(0.055g) ^{1}H n.m.r. δ 1.50,

C3Me, $C4H_3$; 3.48, ClH_2; 7.10, ArH's.

Photolysis of trans-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b)

A solution of trans-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b)(0.521g) in anhydrous deoxygenated benzene(150ml) was irradiated as above for 6hr. The solvent was removed and the ^1H n.m.r. spectrum of the crude reaction product showed the presence of 1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-2-one(139b) δ_H 3.42, ClH_2, 2-(4'-methoxyphenyl)-3-methyl-3-phenylbutanal(140b) δ_H3.65, J 3.5Hz, H2; 9.70, J 3.5Hz, H1, 1-(4'-methoxyphenyl)-2-methyl-2-phenylpropane(142b) δ_H 2.73, ClH_2, 1,2-di-(4'-methoxyphenyl)ethane(143b) δ_H 2.75, ClH_2, $C2H_2$ and unreacted trans-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b) δ_H 3.04, J 2Hz, H2; 3.72, J 2Hz, H1.

The residue was absorbed onto alumina(80g). Elution with light petroleum gave 2,3-dimethyl-2,3-diphenylbutane (141)(0.061g) ^1H n.m.r. δ 1.28, ClMe, $C2H_3$, $C3H_3$, C4Me; 7.08, ArH's. Further elution afforded 1-(4'-methoxyphenyl)-2-methyl-2-phenylpropane(142b)(0.057g) (Found: M^+, 240.1479. $C_{17}H_{20}O$ requires M^+, 240.1513). ^1H n.m.r. δ 1.27, C2Me,$C3H_3$; 2.73, ClH_2; 3,67, ArOMe; 6.57, ClArH's; 7.17, C2ArH's. ^{13}C n.m.r. δ 50.2_4, Cl; 38.8_1, C2; 28.1_3, C2Me, C3; 55.0_7, ArOMe; n.o., Clipso C; 131.2_8, Clortho C; 112.8_8, Clmeta C; n.o., Clpara C; n.o., C2ipso C; 126.2_1, C2ortho C; 127.8_7, C2meta C; 125.7_1, C2para C. Further elution gave 1,2-(4'-methoxyphenyl)ethane(143b)(0.049g) (Found: M^+, 242.1310. $C_{16}H_{18}O_2$ requires M^+, 242.1306). ^1H n.m.r. δ 2.75, ClH_2, $C2H_2$; 3.70, ArOMe; 6.90, Wh/2 20Hz, ArH's. ^{13}C n.m.r. δ 37.2_8, Cl, C2; 55.1_9, ArOMe; 133.9_6, Cl-, C2ipso C; 129.3_6, Cl-, C2ortho C; 113.7_4, Cl-, C2meta C; 157.8_3,

C1-, C2para C.

Elution with light petroleum-ether(20:1) gave trans-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b) (0.049g) ^{1}H n.m.r. δ 1.40, C3Me; 1.50, C4H_3; 3.04, J 2Hz, H2; 3.72, J 2Hz, H1; 3.77, ArOMe; 7.10, Wh/2 31Hz, ArH's and 1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-2-one(139b) (0.032g) (Found: M^+, 268.1486; C, 80.5; H, 7.6. $C_{18}H_{20}O_2$ requires M^+, 268.1462; C, 80.6; H, 7.5%). $\nu_{max}(CCl_4)$ 1715cm^{-1}. λ_{max} 222.2nm(ε11755), 268.5(4204), 274.5(4082), 281.5(3388), 288(1633). ^{1}H n.m.r. δ 1.50, C3Me, C4H_3; 3.42, C1H_2; 3.72, ArOMe; 6.82, C1ArH's; 7.30, C3ArH's. ^{13}C n.m.r. δ 43.1$_0$, C1; 210.3$_1$, C2; 55.1$_2$, C3; 25.0$_3$, C3Me, C4; 55.1$_2$, ArOMe; 127.6$_9$, C1ipso C; 130.3$_7$, C1ortho C; 113.7$_1$, C1meta C; 158.2$_6$, C1para C; 143.6$_2$, C3ipso C; 126.2$_8$, C3ortho C; 128.7$_9$, C3meta C; 127.0$_6$, C3para C.

Photolysis of trans-1,2-epoxy-1-(4'-methylphenyl)-3-methyl-3-phenylbutane(89c)

A solution of trans-1,2-epoxy-1-(4'-methylphenyl)-3-methyl-3-phenylbutane(89c)(0.60g) in anhydrous deoxygenated benzene(160ml) was irradiated(2537Å) as above for 6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of 1-(4'-methylphenyl)-3-methyl-3-phenylbutan-2-one(139c) δ_H 3.32, C1H_2, 2-(4'-methylphenyl)-3-methyl-3-phenylbutanal(140c) δ_H 3.70, J 3Hz, H2; 9.81, J 3Hz, H1, 1-(4'-methylphenyl)-2-methyl-2-phenylpropane(142c) δ_H 2.77, C1H_2, 1,2-di-(4'-methylphenyl)ethane(143c) δ_H 2.81, C1H_2, C2H_2 and unreacted trans-1,2-epoxy-1-(4'-methylphenyl)-3-methyl-3-phenylbutane (89c) δ_H 2.86, J 2Hz, H2; 3.58, J 2Hz, H1.

The residue was absorbed onto alumina(80g). Elution with light petroleum gave 2,3-dimethyl-2,3-diphenylbutane

(141)(0.052g) ^{1}H n.m.r. δ 1.28, Me; 7.08, ArH's. Further elution gave 1-(4'-methylphenyl)-2-methyl-2-phenylpropane (142c)(0.053g) ^{1}H n.m.r. δ 1.30, C2Me, C3H_3; 2.23, ArMe; 2.77, ClH_2; 6.90, Wh/2 15Hz, ArH's. ^{13}C n.m.r. δ 50.6_6, Cl; 38.7_3, C2; 28.1_8, C2Me, C3; 20.9_7, ArMe; 135.7_5, Clipso C; 130.2_8, Clortho C; 128.1_7, Clmeta C; 135.2_1, Clpara C; 149.1_3, C2ipso C; 126.1_8, C2ortho C; 127.8_9, C2meta C; 125.5_4, C2para C. Further elution afforded 1,2-di-(4'-methylphenyl)ethane(143c)(0.042g) (Found: M^+, 210.1342. $C_{16}H_{18}$ requires M^+, 210.1408). ^{1}H n.m.r. δ 2.28, ArMe; 2.81, ClH_2, C2H_2; 6.93, ArH's. ^{13}C n.m.r. δ 37.6_4, Cl, C2; 21.0_0, ArMe; 138.8_7, Cl-, C2ipso C; 128.3_2, Cl-, C2ortho C; 129.0_0, Cl-, C2meta C; 135.2_5, Cl-, C2para C.

Elution with light petroleum-ether(20:1) gave trans-1,2-epoxy-1-(4'-methylphenyl)-3-methyl-3-phenylbutane(89c) (0.147g) ^{1}H n.m.r. δ 1.26, C3Me; 1.35, C4H_3; 2.25, ArMe; 2.86, J 2Hz, H2; 3.58, J 2Hz, H1; 7.15, Wh/2 2Hz, ArH's and 1-(4'-methylphenyl)-3-methyl-3-phenylbutan-2-one(139c) (0.0818g) (Found: M^+, 252.1515. $C_{18}H_{20}O$ requires M^+, 252.1513). $\nu_{max}(CCl_4)$ 1715cm^{-1}. λ_{max} 213nm(ε12249), 263.5(960), 273 (548). ^{1}H n.m.r. δ 1.47, C3Me, C4H_3; 2.27, ArMe; 3.32, ClH_2; 7.05, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 43.6_4, Cl; 210.1_4, C2; 52.7_2, C3; 25.0_3, C3Me, C4; 20.9_8, ArMe; 131.9_4, Clipso C; 129.3_1, Clortho C; 128.9_3, Clmeta C; 136.0_3, Clpara C; 143.6_1, C3ipso C; 126.2_9, C3ortho C; 128.8_2, C3meta C; 127.0_1, C3para C.

Photolysis of trans-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89d)

A solution of trans-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89d)(0.30g) in anhydrous deoxygenated benzene(150ml) was irradiated(2537Å) as above for

6hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the presence of 1-(4'-chlorophenyl)-3-methyl-3-phenylbutan-2-one(139d) δ_H 3.44, ClH_2, 1-(4'-chlorophenyl)-2-methyl-2-phenylpropane(142d) δ_H 2.86, ClH_2, 1,2-di-(4'-chlorophenyl)ethane(143d) δ_H 2.83, ClH_2, $C2H_2$ and unreacted trans-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89d) δ_H 2.81, J 2Hz, H2; 3.55, J 2Hz, H1.

The residue was absorbed onto alumina(80g). Elution with light petroleum gave 2,3-dimethyl-2,3-diphenylbutane (141)(0.025g) ^{1}H n.m.r. δ 1.28, Me; 7.08, ArH's, 1-(4'-chlorophenyl)-2-methyl-2-phenylpropane(142d) ^{1}H n.m.r. δ 1.30, C2Me, $C3H_3$; 2.86, ClH_2; 7.23, ArH's and 1,2-di-(4'-chlorophenyl)ethane(143d) ^{1}H n.m.r. δ 2.83, ClH_2, $C2H_2$; 7.23, ArH's. Elution with light petroleum-ether(20:1) gave 1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89d) (0.048g) ^{1}H n.m.r. δ 1.25, C3Me; 1.35, $C4H_3$; 2.81, J 2Hz, H2; 3.55, J 2Hz, H1; 7.15, Wh/2 7Hz, ArH's and 1-(4'-chlorophenyl)-3-methyl-3-phenylbutan-2-one(139d)(0.010g) (Found: M^+, 272.0950. $C_{17}H_{17}ClO$ requires M^+, 272.0966). $\nu_{max}(CCl_4)$ 1715cm^{-1}. λ_{max} 204nm(ε15878), 221.5(11440), 254.5(493), 264 (394), 276(197). ^{1}H n.m.r. δ 1.52, C3Me, $C4H_3$; 3.44, ClH_2; 7.02, Wh/2 6Hz, ArH's. ^{13}C n.m.r. δ 43.2_9, C1; n.o., C2; 52.7_6, C3; 24.9_3, C3Me, C4; 133.4_4, C1ipso C; 130.7_6, C1ortho C; 128.6_3, C1meta C; n.o., C1para C; n.o., C3ipso C; 126.2_9, C3ortho C; 128.9_2, C3meta C; 127.2_0, C3para C.

Photolysis of trans-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89e)

A solution of trans-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89e)(0.565g) in anhydrous deoxygenated benzene(150ml) was irradiated(2537Å) as above for

6hr. The solvent was removed and the ^1H n.m.r. spectrum of the crude reaction product showed the presence of 1-(3'-chlorophenyl)-3-methyl-3-phenylbutan-2-one(139e) δ_H 3.45, ClH_2, 1-(3'-chlorophenyl)-2-methyl-2-phenylpropane(142e) δ_H 2.78, ClH_2, 1,2-di-(3'-chlorophenyl)ethane(143e) δ_H 2.82, ClH_2, $C2H_2$ and unreacted trans-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89e) δ_H 2.90, J 2Hz, H2; 3.64, J 2Hz, H1.

The residue was absorbed onto alumina(80g). Elution with light petroleum afforded 2,3-dimethyl-2,3-diphenylbutane (141)(0.071g) ^1H n.m.r. δ 1.28, Me; 7.08, ArH's, 1-(3'-chlorophenyl)-2-methyl-2-phenylpropane(142e)(0.031g) ^1H n.m.r. δ 1.30, C2Me, $C3H_3$; 2.78, ClH_2; 7.10, Wh/2 14Hz, ArH's and 1,2-di-(3'-chlorophenyl)ethane(143e)(0.03g) ^1H n.m.r. δ 2.82, ClH_2, $C2H_2$; 7.10, Wh/2 14Hz, ArH's. Further elution with light petroleum-ether(20:1) afforded trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbutane(89e)(0.090g) ^1H n.m.r. δ 1.28, C3Me; 1.35, $C4H_3$; 2.90, J 2Hz, H2; 3.64, J 2Hz, H1; 7.15, Wh/2 14Hz, ArH's and 1-(3'-chlorophenyl)-3-methyl-3-phenylbutan-2-one(139e)(0.073g) (Found: M^+, 272.0942; C, 75.1; H, 6.0. $C_{17}H_{17}ClO$ requires M^+, 272.0966; C, 75.0; H, 6.3%). $\nu_{max}(CCl_4)$ 1715cm^{-1}. λ_{max} 219nm(ε13095), 249(774), 254(833), 260(893), 268(714), 276(536). ^1H n.m.r. δ 1.53, C3Me, $C4H_3$; 3.45, ClH_2; 7.10, Wh/2 2 Hz, ArH's. ^{13}C n.m.r. δ 43.5_3, C1; 209.0_9, C2; 52.7_4, C3; 24.9_0, C3Me, C4; 136.9_0, ClC_1, 129.5_8, ClC_2; 133.9_0, ClC_3; 126.7_1, ClC_4; 129.3_3, ClC_5; 127.6_2, ClC_6; n.o., C3ipso C; 126.2_9, C3ortho C; 128.9_1, C3meta C; 127.1_9, C3para C.

1,2-Epoxy-3-methyl-1,1,3-triphenylbutane(144)

m-Chloroperbenzoic acid(1g) was added to a solution of 3-methyl-1,1,3-triphenylbut-1-ene(131)[58](2g) in ether and the resulting mixture was stirred at 4°C for 4 days. The product was isolated as previously described and after the removal of solvent, the residue was absorbed onto an alumina dry column(80g). Light petroleum-ether(50:1) was allowed to percolate through the column. Elution of segment c. Rf 1 to 0.65 with ether afforded 3-methyl-1,1,3-triphenylbut-1-ene(131)(0.17g) ^{1}H n.m.r. δ 1.30, C3Me, $C4H_3$; 6.37, H2; 7.17, Wh/2 3Hz, ArH's. Elution of segment c. Rf 0.65 to 0.10 with ether gave 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144)(0.97g) (Found: M^+, 314.1614; C, 87.6; H, 7.0. $C_{23}H_{22}O$ requires M^+, 314.1669; C, 87.9; H, 7.1%). $\nu_{max}(CCl_4)$ 1250cm^{-1}. λ_{max} 225(ε2029), 249(286), 254(357), 260(386), 265(300). ^{1}H n.m.r. δ 1.07, C3Me; 1.12, $C4H_3$; 3.50, H2; 7.30,Wh/2 6Hz, ArH's. ^{13}C n.m.r. δ 66.5_0, C1; 74.0_3, C2; 39.2_8, C3; 23.8_3, C3Me; 28.1_3, C4; 142.3_4, 137.3_9, C1ipso C's; 127.7_7, 126.5_1, C1ortho C's; 128.2_5, 128.1_6, C1meta C's; 127.4_6, 127.2_6, C1para C's; 147.5_3, C3ipso C; 125.9_3, C3ortho C; 128.0_6, C3meta C; 126.1_5, C3para C.

Photolysis of 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144)

(i) A solution of 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144)(0.423g) in anhydrous deoxygenated benzene(140ml) in a quartz vessel under a nitrogen atmosphere, was irradiated (2537Å) for 8.5hr and the reaction was monitored by g.l.c. The solvent was removed and the residue absorbed onto alumina(80g). Elution with light petroleum afforded 2,3-dimethyl-2,3-diphenylbutane(141)(0.020g) ^{1}H n.m.r. δ 1.28, Me; 7.08, ArH's and 2-methyl-1,1,2-triphenylpropane(145)

(0.039g) (Found: M^+, 286.1641. $C_{22}H_{22}$ requires M^+, 286.1720). ^1H n.m.r. δ 1.40, C2Me, $C3H_3$; 4.13, H1; 7.12,Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 64.6_5, C1; 42.0_4, C2; 28.5_4, C2Me, C3; 142.2_4, C1ipso C; 130.2_8, C1ortho C; 127.5_9, C1meta C; 127.5_0, C1para C; 147.6_1, C2ipso C; 126.0_3, C2ortho C; 127.3_9, C2meta C; 125.7_1, C2para C. Elution with light petroleum-ether(50:1) gave 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144)(0.111g) ^1H n.m.r. δ 1.07, C3Me; 1.12, $C4H_3$; 3.50, H2; 7.30, Wh/2 6Hz, ArH's. Further elution with light petroleum-ether(5:1) afforded benzophenone(46)(0.067g) $\nu_{max}(CCl_4)$ 1665cm^{-1}. ^1H n.m.r. δ 7.65, Wh/2 14Hz, ArH's.

(ii) A solution of 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144)(0.41g) in anhydrous deoxygenated light petroleum(140ml) was irradiated(2537Å) as above for 7hr. The solvent was removed and the residue absorbed onto alumina(80g). Elution with light petroleum afforded 2,3-dimethyl-2,3-diphenylbutane(141)(0.016g) ^1H n.m.r. δ 1.28, Me; 7.08, ArH's and 2-methyl-1,1,2-triphenylpropane(145) (0.008g) ^1H n.m.r. δ 1.40, C2Me, $C3H_3$; 4.13, H1; 7.30, Wh/2 6Hz, ArH's. Elution with light petroleum-ether(5:1) gave benzophenone(46)(0.022g) $\nu_{max}(CCl_4)$ 1665cm^{-1}. ^1H n.m.r. δ 7.65, Wh/2 14Hz, ArH's.

(iii) A solution of 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144)(0.10g) in anhydrous deoxygenated acetone was irradiated(3000Å) as above for 6.5hr. The solvent was removed and the residue absorbed onto alumina(13g). Nothing could be isolated from this column.

2,3-Diphenyl-1,2-epoxy-3-methylbutane(149)

m-Chloroperbenzoic acid (1g) was added to a solution of 2,3-diphenyl-3-methylbut-1-ene(150)[86](2g) in ether and the resulting mixture was stirred at 4°C for 4 days. The product was isolated as previously descibed and after the removal of solvent, the residue was absorbed onto alumina (80g). Elution with light petroleum afforded 2,3-diphenyl-3-methylbut-1-ene(150)(0.19g) ^{1}H n.m.r. δ 1.42, C3Me, C4H$_3$; 5.13, J 1.5Hz, H1; 5.37, J 1.5Hz, H1'; 7.07, Wh/2 18Hz, ArH's. Elution with light petroleum-ether(100:1) gave 2,3-diphenyl-1,2-epoxy-3-methylbutane(149)(1.84g, m.p.35°C). λ_{max} 215nm(ε4247), 252.8(340), 258.3(383), 263.8(316). ^{1}H n.m.r. δ 1.33, C3Me, C4H$_3$; 2.64, J 5Hz, H1; 3.14, J 5Hz, H1'; 7.13, Wh/2 17Hz, ArH's. ^{13}C n.m.r. δ 50.8$_6$, C1; 66.0$_3$, C2; 40.7$_9$, C3; 24.2$_4$, C3Me; 25.2$_1$, C4; 138.8$_3$, C2ipso C; 126.7$_6$, C2ortho C; 128.2$_9$, C2meta C; 126.0$_4$, C2para C; 145.5$_2$, C3ipso C; 127.2$_6$, C3ortho C; 128.2$_9$, C3meta C; 126.6$_5$, C3para C.

Photolysis of 2,3-diphenyl-1,2-epoxy-3-methylbutane(149)

(i) A solution of 2,3-diphenyl-1,2-epoxy-3-methylbutane(149)(0.6g) in anhydrous deoxygenated benzene(100ml) in a quartz vessel under a nitrogen atmosphere, was irradiated (2537Å) for 8hr and the reaction was monitored by g.l.c. The solvent was removed and the ^{1}H n.m.r. spectrum of the residue showed that no reaction had occurred.

(ii) A solution of 2,3-diphenyl-1,2-epoxy-3-methylbutane(149)(0.6g) and benzophenone(0.1g) in anhydrous deoxygenated benzene(100ml) was irradiated(3000Å) as above for 7hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed that very little

reaction had occurred. The residue was absorbed onto alumina (80g). Elution with light petroleum-ether(100:1) gave 2,3-diphenyl-1,2-epoxy-3-methylbutane(149)(0.59g) ^{1}H n.m.r. δ 1.33, C3Me, $C4H_3$; 2.64, J 5Hz, H1; 3.14, J 5Hz, H1'; 7.13, Wh/2 17Hz, ArH's. Further elution afforded benzophenone(0.1g) and 2,3-diphenyl-3-methylbutanal(140a)(c. 0.008g) ^{1}H n.m.r. δ 1.40, C3Me; 1.45, $C4H_3$; 3.72, J 3Hz, H2; 7.08, Wh/2 3Hz, ArH's; 9.79, J 3Hz, H1.

(iii) A solution of 2,3-diphenyl-1,2-epoxy-3-methylbutane(149)(1.0g) in anhydrous deoxygenated acetone(250ml) was irradiated(3000Å) as above for 8hr. The solvent was removed and the residue absorbed onto alumina(80g). Elution with light petroleum-ether(50:1) afforded 2,3-diphenyl-1,2-epoxy-3-methylbutane(149)(0.445g) ^{1}H n.m.r. δ 1.33, C3Me, $C4H_3$; 2.64, J 5Hz, H1; 3.14, J 5Hz, H1'; 7.13, Wh/2 17Hz, ArH's and 2,2-dimethyl-3,3-diphenyloxetane(151)(0.044g) (Found: M^+, 238.1353. $C_{17}H_{18}O$ requires M^+, 238.1357). $\nu_{max}(CCl_4)$ 1080, 1120cm^{-1}. ^{1}H n.m.r. δ 1.33, C2Me; 5.03, $C4H_2$; 7.17, ArH's. ^{13}C n.m.r. δ 91.0_6, C2; 58.4_0, C3; 76.9_7, C4; 27.4_3, C2Me; 142.8_7, C3ipso C; 128.0_1, C3ortho C; 128.1_7, C3meta C; 126.5_3, C3para C. Further elution gave 2,3-diphenyl-3-methylbutanal(140a)(0.087g) ^{1}H n.m.r. δ 1.40, C3Me; 1.45, $C4H_3$; 3.72, J 3Hz, H2; 7.08, Wh/2 3Hz, ArH's; 9.79, J 3Hz, H1.

Elution with ether afforded 3,3-diphenyl-4-hydroxy-2-methylbut-1-ene(152)(0.073g) (Found: M^+, 238.1353. $C_{17}H_{18}O$ requires M^+, 238.1357). $\nu_{max}(CCl_4)$ 910, 1635, 3580cm^{-1}. ^{1}H n.m.r. δ 1.48, OH; 1.68, C2Me; 4.36, $C4H_2$; 4.85, H1; 5.16, H1'; 7.26, ArH's. ^{13}C n.m.r. δ 116.1_2, C1; n.o. C2; 59.9_4, C3; 68.5_3, C4; 21.5_6, C2Me; 143.0_2, C3ipso C; 129.3_5, C3ortho C; 128.1_9, C3meta C; 126.6_4, C3para C and

2,3-diphenyl-3-methylbutan-1-ol(153a)(0.052g) ^{1}H n.m.r. δ 1.20, C3Me; 1.28, $C4H_3$; 3.08, J 5Hz, J 10Hz, H2; 3.77, Wh/2 15Hz, $C1H_2$; 7.19, Wh/2 3Hz, ArH's.

3,3-Dimethyl-4,5-epoxy-1,1,5,5-tetraphenylpent-1-ene(154)

A solution of monoperphthalic acid[117](0.3M, 10ml) in ether was added to a solution of 3,3-dimethyl-1,1,5,5-tetraphenylpenta-1,4-diene(3)[3](0.91g) in ether and the resulting mixture was stirred at 4°C for 4 days. Sodium bicarbonate and water were added and the resulting mixture was stirred for 5min. The organic layer was separated, washed with sodium bicarbonate solution and dried over anhydrous magnesium sulphate. The solvent was removed and the residue absorbed onto alumina(80g). Elution with light petroleum gave 3,3-dimethyl-1,1,5,5-tetraphenylpenta-1,4-diene(3)(0.186g) ^{1}H n.m.r. δ 1.05, C3Me; 5.97, H2, H4; 7.12, Wh/2 ArH's. Elution with light petroleum-ether(20:1) afforded 3,3-dimethyl-4,5-epoxy-1,1,5,5-tetraphenylpent-1-ene (154)(0.41g). ν_{max}(neat) 760, 1250cm^{-1}. λ_{max} 212nm(ε32597), 252(13812), 294(737). ^{1}H n.m.r. δ 0.77, C3Me; 0.90, C3Me; 3.07, H4; 5.85, H2; 7.25, ArH's. ^{13}C n.m.r. δ 139.7_8, C1; 134.3_2, C2; 38.0_8, C3; 75.1_6, C4; 66.2_0, C5; 143.3_9, 140.5_6, C1ipso C's; 130.0_6, 126.6_9, C1ortho C's; 127.7_7, 127.6_7, C1meta C's; 126.7_9, 126.6_0, C1para C's; 142.1_7, 137.3_9, C5ipso C's; 127.9_1, 126.3_5, C5ortho C's; 128.5_3, 128.1_6, C5meta C's; 127.4_8, 127.3_8, C5para C's; 27.0_7, C3Me.

Further elution with light petroleum-ether(5:1) afforded 1,2-4,5-diepoxy-3,3-dimethyl-1,1,5,5-tetraphenylpentane(155)(0.14g). $\nu_{max}(CCl_4)$ 1260cm^{-1}. ^{1}H n.m.r. δ 0.59,

C3Me; 0.78, C3Me; 2.95, H2, H4; 7.18, ArH's. ^{13}C n.m.r. δ 66.2_2, C1, C5; 72.3_0, C2, C4; 37.5_5, C3; 20.4_1, 21.8_7, C3Me; 141.9_4, 137.4_8, C1-, C5ipso C's; 127.9_2, 126.4_8, C1-, C5ortho C's; 128.2_6, 128.1_7, C1-, C5meta C's; 127.5_7, 127.4_5, C1-, C5para C's.

NOTE: The diepoxide(155) decomposed rapidly at room temperature and over a period of two days at $4^{o}C$. The monoepoxide(154) decomposed over a period of 24hr at room temperature and was also unstable at $4^{o}C$.

Photolysis of 3,3-dimethyl-4,5-epoxy-1,1,5,5-tetraphenyl-pent-1-ene(154)

(i) A solution of 3,3-dimethyl-4,5-epoxy-1,1,5,5-tetraphenylpent-1-ene(154)(0.24g) in anhydrous deoxygenated benzene(200ml), in a quartz vessel under a nitrogen atmosphere, was irradiated(2537Å) and the reaction was monitored by g.l.c. and t.l.c. After 3.5hr the solvent was removed and the ^{1}H n.m.r. spectrum of the residue showed that no epoxide remained. The i.r. spectrum showed the presence of some carbonyl compounds ν 1720, 1665cm^{-1}. The residue was absorbed onto alumina(80g). Elution afforded nothing in sufficient quantity to be identified.

(ii) A solution of 3,3-dimethyl-4,5-epoxy-1,1,5,5-tetraphenylpent-1-ene(154)(0.54g) in anhydrous deoxygenated light petroleum(300ml) was irradiated(2537Å) as above for 2hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the residue showed that little reaction had occurred. The oil was taken up in anhydrous light petroleum(300ml), deoxygenated for 0.5hr and irradiated for 7hr. The solvent was removed and the ^{1}H n.m.r. spectrum showed the presence of a significant amount of an aldehyde δ_H 4.75, J 2.5Hz;

9.33, J 2.5Hz; ν_{max} 1725, 2720cm^{-1}. The residue was absorbed onto alumina(80g). Elution afforded benzophenone(46)(0.06g). $\nu_{max}(CHCl_3)$ 1665cm^{-1}, ^{1}H n.m.r. δ 7.65, Wh/2 14Hz, ArH's, as the only identifiable product.

3,3-Dimethyl-1,1,5-triphenylpenta-1,4-diene(158)

Freshly cut lithium was added to a cold, stirred solution of n-butyl bromide(4ml) in anhydrous ether and the resulting mixture was stirred for 3hr at less than 15°C. The butyl-lithium solution was added to a rapidly stirred suspension of benzyltriphenylphosphonium chloride in dry ether under a nitrogen atmosphere and the resulting mixture was stirred at room temperature for 2.5hr. A solution of 2,2-dimethyl-4,4-diphenylbut-3-enal(159)[4](4g) in anhydrous benzene was added to the above solution and the resulting mixture was heated under reflux for 3hr and stirred at room temperature overnight. The precipitate was filtered and washed with benzene. The solvent was removed and the residue absorbed onto alumina(160g). Elution with light petroleum gave a mixture(1:1) of cis- and trans-3,3-dimethyl-1,1,5-triphenylpenta-1,4-diene(158)(2.26g). The oil was absorbed onto silver nitrate alumina(80g) which failed to separate the isomers.

cis-3,3-Dimethyl-1,1,5-triphenylpenta-1,4-diene(158-cis) $\nu_{max}(CCl_4)$ 680, 1670cm^{-1}. ^{1}H n.m.r. δ 1.05, C3Me; 5.45, J 12Hz, H4; 6.02, H2; 6.19, J 12Hz, H5; 7.20, Wh/2 4Hz, ArH's. ^{13}C n.m.r. δ 142.0_1, C1; 138.8_9, C2; 38.9_9, C3; 142.0_1, C4; 130.1_0, C5; 30.9_3, C3Me; 143.6_7, 140.7_4, C1ipso C's; 130.1_0, 126.7_8, C1ortho C's; 127.7_9, 127.6_4, C1meta C's; 126.4_9, 126.3_4, C1para C's; 138.4_1, C5ipso C; 127.6_4, C5ortho C; 128.6_8, C5meta C; 126.7_8, C5para C.

trans-3,3-Dimethyl-1,1,5-triphenylpenta-1,4-diene (158-trans) ^{1}H n.m.r. δ 1.15, C3Me; 6.09, H4, H5; 6.11, H2; 7.20, ArH's.

Epoxidation of cis- and trans-3,3-dimethyl-1,1,5-triphenylpenta-1,4-diene(158)

A solution of monoperphthalic acid(0.07M, 100ml) in ether was added to a solution of cis- and trans-3,3-dimethyl-1,1,5-triphenylpenta-1,4-diene(158)(2g) in ether and the resulting mixture was stirred at 4°C for 8 days. The residue isolated as above was absorbed onto alumina(80g). Elution with light petroleum afforded a mixture of cis- and trans-3,3-dimethyl-1,1,5-triphenylpenta-1,4-diene(158) (0.78g) cis: ^{1}H n.m.r. δ 1.05, C3Me; 5.45, J 12Hz, H4; 6.02, H2; 6.19, J 12Hz, H5; 7.20, ArH's. trans: ^{1}H n.m.r. δ 1.15, C3Me; 6.09, H4, H5; 6.11, H2; 7.20, ArH's.

Elution with light petroleum-ether(100:1) gave cis-3,3-dimethyl-4,5-epoxy-1,5,5-triphenylpent-1-ene(161-cis)(0.286g) ν_{max}(neat) 710, 1250cm^{-1}. λ_{max} 221nm(ε99071), 248(113003), 293.5(13622). ^{1}H n.m.r. δ 0.79, 0.92, C3Me; 3.19, H4; 5.34, J 13Hz, H2; 6.24, J 13Hz, H1; 7.08, ClArH's; 7.22, C5ArH's. ^{13}C n.m.r. δ 128.4_5, C1; 137.0_4, C2; 38.4_1, C3; 74.6_5, C4; 66.5_0, C5; 26.5_5, 26.8_5, C3Me; 142.1_2, 137.4_9, 137.0_4, C1-, C5ipso C's; 127.8_1, 127.4_4, 126.4_5, C1-, C5ortho C's; 128.7_5, 128.5_6, 128.2_1, C1-, C5meta C's; 127.5_7, 126.3_5, C1-, C5para C's.

Further elution gave trans-3,3-dimethyl-4,5-epoxy-1,5,5-triphenylpent-1-ene(161-trans)(0.0301g) ν_{max}(neat) 970, 1250cm^{-1}. ^{1}H n.m.r. δ 0.97, 1.11, C3Me; 3.22, H4; 6.00, H2; 6.05, H1; 7.15, C5ArH's; 7.27, ClArH's. ^{13}C n.m.r. δ 127.8_2, C1; 135.5_6, C2; 37.7_2, C3; 73.8_0, C4; 66.6_2, C5; 25.0_9, 25.3_7, C3Me; 142.2_1, 137.6_2, 137.4_3, C1-, C5ipso C's;

127.9_1, 126.9_2, 126.4_9, C1-, C5ortho C's; 128.2_8, 128.2_2, C1-, C5meta C's; 127.5_1, 127.4_2, 126.1_9, C1-, C5para C's.

Further elution gave trans-3,3-dimethyl-4,5-epoxy-1,1,5-triphenylpen-1-ene(160-trans)(0.060g) $\nu_{max}(CCl_4)$ 850, 890, 1260, 1665cm^{-1}. λ_{max} 215nm(ε22320), 249(9251), 291 (1322), 305.5(808), 321(441). ^1H n.m.r. δ 0.95, 1.00, C3Me; 2.80, J 2Hz, H4; 3.63, J 2Hz, H5; 6.03, H2; 7.10, Wh/2 12Hz, ArH's. ^{13}C n.m.r. δ 140.3_2, C1; 134.2_7, C2; 37.6_0, C3; 69.7_3, C4; 56.0_0, C5; 24.6_7, 25.9_4, C3Me; 143.5_5, 141.8_9, C1ipso C's; 130.0_3, 126.9_6, C1ortho C's; 128.0_3, 127.8_2, C1meta C's; 125.6_9, 125.4_8, C1para C's; 137.7_5, C5ipso C; 126.9_6, C5ortho C; 128.5_1, C5meta C; 127.9_2, C5para C.

Further elution gave cis-3,3-dimethyl-4,5-epoxy-1,1,5-triphenylpent-1-ene(160-cis)(0.12g) ^1H n.m.r. δ 0.75, C3Me; 2.95, J 4Hz, H4; 3.95, J 4Hz, H5; 5.75, H2; 7.15, Wh/2 12Hz, ArH's.

Elution with light petroleum-ether(10:1) afforded trans-1,2-4,5-diepoxy-3,3-dimethyl-1,1,5-triphenylpentane (162-trans)(0.10g) ^1H n.m.r. δ 0.78, 1.00, C3Me; 2.59, J 2Hz, H4; 3.30, H2; 3.78, J 2Hz, H5; 7.15, ArH's, cis-1,2-4,5-diepoxy-3,3-dimethyl-1,1,5-triphenylpentane(162-cis) (0.06g) ^1H n.m.r. δ 0.55, 0.71, C3Me; 2.90, J 4Hz, H4; 2.92, H2; 3.95, J 4Hz, H5; 7.25, ArH's and trans-1,2-4,5-diepoxy-3,3-dimethyl-1,1,5-triphenylpentane(162-trans)(0.04g) ^1H n.m.r. δ 0.72, 0.92, C3Me; 2.92, J 2Hz, H4; 3.32, H2; 3.62, J 2Hz, H5; 7.25, ArH's.

The diepoxides(162) were unstable at 4^oC therefore further data are not available. The monoepoxides(160, 161) could only be partially separated. They were unstable at room temperature and decomposed over a period of two weeks at 4^oC.

Photolysis of cis-3,3-dimethyl-4,5-epoxy-1,5,5-triphenylpent-1-ene(161-cis)

A solution of cis-3,3-dimethyl-4,5-epoxy-1,5,5-triphenylpent-1-ene(161-cis)(0.14g) in anhydrous deoxygenated light petroleum(150ml) was irradiated(2537Å) as above for 11hr and the reaction was monitored by g.l.c. The solvent was removed and the residue absorbed onto alumina(13g). Elution afforded benzophenone(46)(0.009g) ν_{max} 1665cm^{-1}, ^{1}H n.m.r. δ 7.65, Wh/2 14Hz, ArH's, as the only identifiable product.

Photolysis of cis- and trans-3,3-dimethyl-4,5-epoxy-1,1,5-triphenylpent-1-ene(160)

A solution of cis- and trans-3,3-dimethyl-4,5-epoxy-1,1,5-triphenylpent-1-ene(160)(0.17g, c. 2:1) in anhydrous deoxygenated benzene(100ml) was irradiated(2537Å) as above for 5hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed the cis and trans epoxides(160) in a ratio of 3:1. No further reaction was detected. The residue was absorbed onto alumina(13g). Elution with light petroleum-ether(100:1) afforded cis-3,3-dimethyl-4,5-epoxy-1,1,5-triphenylpent-1-ene(160-cis) (0.052g) ^{1}H n.m.r. δ 0.75, C3Me; 2.95, J 4Hz, H4; 3.95, J 4Hz, H5; 5.75, H2; 7.15, Wh/2 12Hz, ArH's.

1,1-Diphenyl-4,5-epoxy-3,3,5-trimethylhex-1-ene(163)

A solution of monoperphthalic acid(0.19M, 10ml) was added to a solution of 1,1-diphenyl-3,3,5-trimethylhexa-1,4-diene(5)[4](0.26g) in ether and the resulting mixture was stirred at 4°C for 8 days. The product, isolated as above, was absorbed onto alumina(80g). Elution with light petroleum gave 1,1-diphenyl-3,3,5-trimethylhexa-1,4-diene(5)(0.043g)

^{1}H n.m.r. δ 1.10, C3Me; 1.47, J 1.5Hz, C5Me; 1.67, J 1.5Hz, $C6H_3$; 5.00, H4; 6.19, H2; 7.14, ArH's. Elution with light petroleum-ether(20:1) afforded 1,1-diphenyl-4,5-epoxy-3,3,5-trimethylhex-1-ene(163)(0.136g) $\nu_{max}(CCl_4)$ 1245, 1730cm^{-1}. λ_{max} 211nm(ε17714), 248.5(14476), 292.5(476). ^{1}H n.m.r. δ 0.92, C5Me; 1.12, C3Me; 1.37, $C6H_3$; 2.52, H4; 6.12, H2; 7.07, ArH's. ^{13}C n.m.r. δ 139.1_9, C1; 134.9_1, C2; 37.2_1, C3; 72.8_0, C4; 59.1_4, C5; 18.8_4, C5Me; 26.4_3, C6; 26.6_2, 28.9_3, C3Me; 143.7_6, 140.8_2, C1ipso C's; 130.1_2, 126.8_5, C1ortho C's; 128.0_3, 127.8_7, C1meta C's; 126.9_7, 126.7_5, C1para C's.

Photolysis of 1,1-diphenyl-4,5-epoxy-3,3,5-trimethylhex-1-ene(163)

(i) A solution of 1,1-diphenyl-4,5-epoxy-3,3,5-trimethylhex-1-ene(163)(0.10g) in anhydrous deoxygenated light petroleum(100ml) was irradiated(2537Å) as above for 10hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the residue showed that little reaction had occurred. The residue was absorbed onto alumina(13g). Elution with light petroleum-ether(100:1) afforded 1,1-diphenyl-4,5-epoxy-3,3,5-trimethylhex-1-ene(163)(0.086g) ^{1}H n.m.r. δ 0.92, C5Me; 1.12, C3Me; 1.37, $C6H_3$; 2.52, H4; 6.12, H2; 7.07, ArH's.

(ii) A solution of 1,1-diphenyl-4,5-epoxy-3,3,5-trimethylhex-1-ene(163)(0.10g) in anhydrous deoxygenated acetone(100ml) was irradiated(3000Å) as above for 5hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the crude reaction product showed that some reaction had occurred. The residue was absorbed onto alumina(13g). Elution with light petroleum-ether(100:1) afforded 1,1-diphenyl-4,5-epoxy-3,3,5-trimethylhex-1-ene(163)(0.052g) ^{1}H n.m.r.

δ 0.92, C5Me; 1.12; C3Me; 1.37, $C6H_3$; 2.52, H4; 6.12, H2; 7.07, ArH's. Further elution afforded an unidentified product(0.030g) which appeared to be a mixture of two isomers. $\nu_{max}(CCl_4)$ 890, 900, 1030, 1260, 1450. ^1H n.m.r. δ 0.68, 0.70, 0.80, 1.03, 1.15, 1.17, 1.30, 1.43, Me; 2.23, 2.51, 3.13, 3.22, CH; 7.23, Wh/2 5Hz, ArH's. ^{13}C n.m.r. δ 19.3_4, 19.6_9, 21.3_8, 21.9_7, 22.6_2, 23.7_5, 26.7_8, Me; 35.8_0, 36.3_3, 58.2_8, 59.7_2, 66.6_1, 69.7_8, C_q; 69.7_8, 70.4_8, 71.4_5, 72.8_9, CH; 128.2_8, 128.1_2, 128.0_2, 127.5_7, 126.6_2, 126.4_2, ArC's.

4,5-Epoxy-1-phenyl-3,3,5-trimethylhex-1-ene(166)

A solution of monoperphthalic acid(0.07M, 120ml) in ether was added to a solution of cis- and trans-1-phenyl-3,3,5-trimethylhexa-1,4-diene(13g)[7](1.66g) in ether and the resulting mixture was stirred at 4°C for 12 days. The residue, isolated as above, was absorbed onto alumina(80g). Elution with light petroleum gave cis- and trans-1-phenyl-3,3,5-trimethylhexa-1,4-diene(13)(0.79g) cis: ^1H n.m.r. δ 1.16, C3Me; 1.40, J 1.5Hz, C5Me; 1.52, J 1.5Hz, $C6H_3$; 5.13, Wh/2 5Hz, H4; 5.73, J 13Hz, H2; 6.26, J 13Hz, H1; 7.17, ArH's. trans: ^1H n.m.r. δ 1.21, C3Me; 1.60, J 1.5Hz, C5Me; 1.76, J 1.5Hz, $C6H_3$; 5.21, Wh/2 5Hz, H4; 6.26, H1, H2; 7.23, Wh/2 6Hz, ArH's.

Elution with light petroleum-ether(50:1) afforded cis-4,5-epoxy-1-phenyl-3,3,5-trimethylhex-1-ene(166-cis) (0.25g) (Found: M^+, 216.1496. $C_{15}H_{20}O$ requires M^+, 216.1513). $\nu_{max}(CCl_4)$ 700, 1230, 1640cm^{-1}. λ_{max} 206.5nm(ε7786), 226 (3990). ^1H n.m.r. δ 1.03, C5Me; 1.06, $C6H_3$; 1.10, C3Me; 1.33, C3Me; 2.54, H4; 5.60, J 12.5Hz, H2; 6.42, J 12.5Hz, H1; 7.20, ArH's. ^{13}C n.m.r. δ 128.1_5, C1; 138.2_3, C2; 37.4_0, C3; 72.3_1, C4; 59.3_6, C5; 18.9_5, C5Me; 26.2_2, C6; 27.9_3,

28.3_2, C3Me; 139.1_0, Clipso C; 127.7_9, Clortho C; 128.7_1; Clmeta C; 126.5_2, Clpara C. Further elution afforded trans-4,5-epoxy-1-phenyl-3,3,5-trimethylhex-1-ene(166-trans)(0.25g) $\nu_{max}(CCl_4)$ 970, 1230, 1650cm^{-1}. λ_{max} 209.5nm(ε13631), 248.5 (11398), 284(1034), 292.5(705). ^{1}H n.m.r. δ 1.13, C3Me; 1.33, C5Me; 1.36, C3Me; $C6H_3$; 2.62, H4; 6.28, H1, H2; 7.30, Wh/2 6Hz, ArH's. ^{13}C n.m.r. δ 127.0_7, C1; 136.5_1, C2; 37.0_1, C3; 71.9_3, C4; 59.3_2, C5; 18.9_8, C5Me; 24.4_3, C6; 26.6_9, 28.0_7, C3Me; 137.7_8, Clipso C; 126.1_6, Clortho C; 128.5_5, Clmeta C; 126.3_1, Clpara C.

Photolysis of cis- and trans-4,5-epoxy-1-phenyl-3,3,5-trimethylhex-1-ene(166)

(i) A solution of cis- and trans-4,5-epoxy-1-phenyl-3,3,5-trimethylhex-1-ene(166)(0.09g, c. 4:11) in anhydrous deoxygenated benzene(100ml) was irradiated(2537Å) as above for 4hr and the reaction was monitored by g.l.c. The solvent was removed and the ^{1}H n.m.r. spectrum of the reaction product showed the presence of the cis and trans epoxides (166)(c. 1:1) by integration of the peaks at δ_H 2.54, 5.60, 6.42 and δ_H 2.62, 6.28 respectively. No further reaction could be detected.

(ii) A solution of cis- and trans-4,5-epoxy-1-phenyl-3,3,5-trimethylhex-1-ene(166)(0.30g, c. 1:1) in anhydrous deoxygenated acetone(300ml) was irradiated(3000Å) as above for 5.5hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the reaction product showed the presence of the cis and trans epoxides(166) in a ratio c. 2:1, by integration of the peaks at δ_H 2.54, 5.60, 6.42 and δ_H 2.62, 6.28 respectively.

Epoxidation of 3,3-dimethyl-1,1,4-triphenylpenta-1,4-diene(167)

m-Chloroperbenzoic acid(0.07g) was added to a solution of 3,3-dimethyl-1,1,4-triphenylpenta-1,4-diene(167)[87](0.32g) in ether and the resulting mixture was stirred at 4°C for 4 days. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum gave 3,3-dimethyl-1,1,4-triphenylpenta-1,4-diene(167)(0.14g) ^{1}H n.m.r. δ 1.05, C3Me; 4.78, J 1.5Hz, H5; 5.03, J 1.5Hz, H5'; 6.07, H2; 7.10, Wh/2 6Hz, ArH's.

Further elution afforded 3,3-dimethyl-4,5-epoxy-2,5,5-triphenylpent-1-ene(169)(0.076g) $\nu_{max}(CCl_4)$ 890, 1260, 1660cm^{-1}. λ_{max} 214nm(ε17587), 218(16911), 247.5(2931). ^{1}H n.m.r. δ 0.65, 1.00, C3Me; 3.37, H4; 4.96, J 1.5Hz, H1; 5.39, J 1.5Hz, H1'; 7.31, Wh/2 8Hz, ArH's. ^{13}C n.m.r. δ 113.8_9, C1; 156.6_0, C2; 41.3_2, C3; 73.6_0, C4; 66.5_8, C5; 26.8_2, 22.1_0, C3Me; 142.3_0, 137.5_6, C2-, C5ipso C's; 128.9_7, 128.2_1, C2-, C5meta C's; 127.7_0, 127.5_1, 127.3_5, 126.7_3, 126.1_9, C2-, C5ortho C's, C2-, C5para C's.

Elution with light petroleum-ether(200:1) gave 3,3-dimethyl-4,5-epoxy-1,1,4-triphenylpent-1-ene(168)(0.052g) $\nu_{max}(CCl_4)$ 835, 1260, 1670cm^{-1}. λ_{max} 215.5nm(ε18537), 248.5(14472). ^{1}H n.m.r. δ 0.89, C3Me; 2.61, J 5Hz, H5; 3.03, J 5Hz, H5'; 6.10, H2; 7.10, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 139.4_8, C1; 134.6_8, C2; 40.8_0, C3; 66.4_8, C4; 51.2_8, C5; 25.0_3, 25.4_2, C3Me; 143.7_2, 140.6_9, 140.3_0, C1-, C4ipso C's; 129.9_0, 127.3_5, 126.8_7, C1-, C4ortho C's; 128.7_8, 128.0_4, 127.5_6, C1-, C4meta C's; 128.2_3, 126.7_9, C1-, C4para C's.

Elution with light petroleum-ether(100:1) afforded 1,2-4,5-diepoxy-3,3-dimethyl-1,1,4-triphenylpentane(170) (0.034g) $\nu_{max}(CCl_4)$ 1260cm^{-1}. λ_{max} 212nm(ε12781), 249(2308). ^{1}H n.m.r. δ 0.67, 0.75, C3Me; 2.68, J 5Hz, H5; 3.16, J 5Hz, H5'; 3.32, H2; 7.20, Wh/2 4Hz, ArH's. ^{13}C n.m.r. δ 65.7_6,

C1; 71.5_9, C2; 39.4_5, C3; 65.8_5, C4; 50.9_6, C5; 19.5_8, 21.5_7, C3Me; 138.8_5, 138.7_6, 137.6_7, C1-, C4ipso C's; 128.9_0, 128.2_6, 128.1_1, 127.8_1, 127.6_7, 127.5_9, 127.4_8, 127.3_8, C1-, C4ortho C's, C1-, C4meta C's, C1para C's.

Photolysis of 3,3-dimethyl-4,5-epoxy-2,5,5-triphenyl-pent-1-ene(169)

(i) A solution of 3,3-dimethyl-4,5-epoxy-2,5,5-triphenylpent-1-ene(169)(0.163g) in anhydrous deoxygenated benzene(150ml) was irradiated(2537Å) as above for 8hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the reaction product showed that no significant reaction had occurred. The residue was absorbed onto alumina(13g). Elution with light petroleum-ether(50:1) gave 3,3-dimethyl-4,5-epoxy-2,5,5-triphenylpent-1-ene(169)(0.13g) ^{1}H n.m.r. δ 0.65, 1.00, C3Me; 3.37, H4; 4.96, J 1.5Hz, H1; 5.39, J 1.5Hz, H1'; 7.31, Wh/2 8Hz, ArH's.

(ii) A solution of 3,3-dimethyl-4,5-epoxy-2,5,5-triphenylpent-1-ene(169)(0.15g) in anhydrous deoxygenated acetone(150ml) was irradiated(3000Å) as above for 6hr. The solvent was removed and the residue absorbed onto alumina (13g). Elution with light petroleum-ether(50:1) afforded 3,3-dimethyl-4,5-epoxy-2,5,5-triphenylpent-1-ene(169)(0.029g) ^{1}H n.m.r. δ 0.65, 1.00, C3Me; 3.37, H4; 4.96, J 1.5Hz, H1; 5.39, J 1.5Hz, H1'; 7.31, Wh/2 8Hz, ArH's. Further elution afforded 3,3-dimethyl-2,5,5-triphenylpent-1-en-4-one(171) (0.030g) $\nu_{max}(CCl_4)$ 900, 1660, 1710cm^{-1}. ^{1}H n.m.r. δ 1.22, C3Me; 5.29, H1; 5.31, H1'; 5.57, H5; 7.13, Wh/2 10Hz, ArH's. ^{13}C n.m.r. δ 117.2_0, C1; n.o., C2; 54.8_6, C3; 210.3_9, C4; 57.8_6, C5; 25.3_5, C3Me; 152.7_1, C5ipso C's; 140.1_0, C2ipso C; 128.5_2, 127.2_0, 126.8_1, C2-, C5ortho C's, C2-, C5meta C's,

C2-, C5*para* *C*'s. Further elution gave benzophenone(46)(0.029g) $\nu_{max}(CHCl_3)$ 1665cm^{-1}, ^{1}H n.m.r. δ 7.65, Wh/2 14Hz, ArH's.

Photolysis of 3,3-dimethyl-4,5-epoxy-1,1,4-triphenyl-pent-1-ene(168)

(i) A solution of 3,3-dimethyl-4,5-epoxy-1,1,4-triphenylpent-1-ene(168)(0.11g) in anhydrous deoxygenated benzene(150ml) was irradiated(2537Å) as above for 11hr. The solvent was removed and the reaction product showed the presence of the epoxide(168) only. The residue was absorbed onto alumina(13g). Elution with light petroleum-ether(50:1) gave 3,3-dimethyl-4,5-epoxy-1,1,4-triphenyl-pent-1-ene(168)(0.087g) ^{1}H n.m.r. δ 0.89, C3Me; 2.61, J 5Hz, H5; 3.03, J 5Hz, H5'; 6.10, H2; 7.10, Wh/2 3Hz, ArH's.

(ii) A solution of 3,3-dimethyl-4,5-epoxy-1,1,4-triphenylpent-1-ene(168)(0.10g) in anhydrous deoxygenated acetone(100ml) was irradiated(3000Å) as above for 8hr. The solvent was removed and the ^{1}H n.m.r. spectrum of the reaction product showed the presence of an aldehyde (*c*. 40%) δ_H 9.97, Wh/2 4Hz, CHO; 3.47, Wh/2 4Hz; $\nu_{max}(CCl_4)$ 1720,2720cm^{-1}. The residue was absorbed onto alumina(13g). Elution of the column gave nothing in suffient quantity to be identified.

Reaction of trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a) with BF_3-etherate in benzene

BF_3-etherate(0.5ml) was added to a solution of trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a) (0.2g) in benzene(15ml) and the resulting mixture was stirred for 2 min. Saturated potassium carbonate solution was added and the mixture was stirred for 15 min. The solution was dried over anhydrous potassium carbonate. The solvent was removed and the residue absorbed onto alumina(13g). Elution with light petroleum-ether(50:1) gave 2,3-diphenyl-3-methylbutanal(140a)(0.09g) (Found: M^+, 238.1353. $C_{17}H_{18}O$ requires M^+, 238.1358). ν_{max}(neat) 1715, 2720cm^{-1}. ^1H n.m.r. δ 1.40, C3Me; 1.45, $C4H_3$; 3.72, J 3Hz, H2; 7.08, Wh/2 3Hz, ArH's; 9.79, J 3Hz, H1. ^{13}C n.m.r. δ 201.7_8, C1; 68.6_7, C2; 41.2_0, C3; 25.7_0, C3Me; 27.7_7, C4; 134.5_9, C2ipso C; 130.6_0, C2ortho C; 127.9_8, C2meta C; 127.3_2, C2para C; 146.1_7, C3ipso C; 126.6_4, C3ortho C; 128.1_0, C3meta C; 126.4_0, C3para C.

Further elution with light petroleum-ether(20:1) afforded 1R*,2R*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(189a)(0.03g) (Found: M^+, 284.1770; C, 79.9; H, 8.1. $C_{19}H_{24}O_2$ requires M^+, 284.1776; C, 80.2; H, 8.5%). ν_{max}(CCl_4) 1065, 1090, 1110, 3575cm^{-1}. ^1H n.m.r. δ 1.03, J 7Hz, OCH_2Me; 1.28, OH; 1.35, C3Me; 1.40, $C4H_3$; 3.15, Wh/2 17Hz, OCH_2Me; 3.64, Wh/2 6Hz, H2; 3.90, J 2Hz, H1; 7.18, Wh/2 11Hz, ArH's. ^{13}C n.m.r. δ 79.2_3, C1; 82.4_0, C2; 42.7_9, C3; 22.5_2, C3Me; 27.1_9, C4; 15.1_8, OCH_2Me; 63.9_7, OCH_2Me; 141.5_3, C1ipso C; 126.6_0, C1ortho C; 128.1_2, C1meta C; 127.4_4, C1para C; 147.1_6, C3ipso C; 126.6_0, C3ortho C; 128.2_3, C3meta C; 126.0_4, C3para C.

Reaction of 2,3-diphenyl-3-methylbutanal(140a) with lithium aluminium hydride

Boron trifluoride etherate(0.5ml) was added to a solution of trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a) (0.3g) in benzene(15ml) and the resulting mixture was stirred for 5 min. The crude reaction mixture, isolated as above, was taken up in dry ether and added to a stirred suspension of lithium aluminium hydride(0.01g)[119] in dry ether. The resulting mixture was heated under reflux for 0.5hr and after cooling, sodium sulphate and water were added. The ethereal layer was separated and washed with 10% sulphuric acid. The solution was dried over anhydrous magnesium sulphate and filtered. The solvent was removed and the residue absorbed onto alumina(13g). Elution with light petroleum-ether(20:1) gave 1R*,2R*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(189a)(0.056g) ^{1}H n.m.r. δ 1.03, J 7Hz, $OCH_2\underline{Me}$; 1.28, OH; 1.35, C3Me; 1.40, $C4H_3$; 3.15, Wh/2 17Hz, $O\underline{CH_2}Me$; 3.64, Wh/2 6Hz, H2; 3.90, J 2Hz, H1; 7.18, Wh/2 11Hz, ArH's.

Further elution with light petroleum-ether(5:1) gave 2,3-diphenyl-3-methylbutan-1-ol(153a)(0.12g) (Found: M^+, 240.1481; C, 85.0; H, 8.7. $C_{17}H_{20}O$ requires M^+, 240.1509; C, 85.0; H, 8.4%). ν_{max}(neat) 3620cm^{-1}. ^{1}H n.m.r. δ 1.20, C3Me; 1.28, $C4H_3$; 1.40, OH; 3.08, J 5Hz, J 10Hz, H2; 3.77, Wh/2 15Hz, ClH_2; 7.19, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 62.5_8, C1; 59.4_5, C2; 40.1_2, C3; 24.0_5, C3Me; 28.9_9, C4; 139.2_4, C2ipso C; 130.1_0, C2ortho C; 127.9_1, C2meta C; 126.7_8, C2para C; 148.0_7, C3ipso C; 126.3_0, C3ortho C; 128.0_1, C3meta C; 125.8_9, C3para C.

trans-1-d-1,3-diphenyl-1,2-epoxy-3-methylbutane(190a)

m-Chloroperbenzoic acid(0.4g) was added to a solution of trans-1-d-1,3-diphenyl-3-methylbut-1-ene(110a)(0.5g) in ether and the resulting mixture was stirred at room temperature for 24hr. Sodium bicarbonate and water were added and the resulting mixture was stirred for 15 min. The ethereal layer was washed with sodium bicarbonate solution and dried over anhydrous magnesium sulphate. The solvent was removed and the residue absorbed onto alumina (80g). Elution with light petroleum gave trans-1-d-1,3-diphenyl-3-methylbut-1-ene(110a)(0.087g) ^{1}H n.m.r. δ 1.50, C3Me, $C4H_3$; 6.40, Wh/2 6Hz, H2; 7.26, Wh/2 5Hz, ArH's. Further elution with light petroleum-ether(50:1) afforded trans-1-d-1,3-diphenyl-1,2-epoxy-3-methylbutane(190a)(0.30g, m.p. 40-42^{o}C) (Found: M^{+}, 239.1472. $C_{17}H_{17}DO$ requires M^{+}, 239.1416). $\nu_{max}(CCl_4)$ 895cm^{-1}. ^{1}H n.m.r. δ 1.32, C3Me; 1.40, $C4H_3$; 3.05, H2; 7.25, Wh/2 2Hz, ArH's. ^{13}C n.m.r. δ 69.8_9, C2; 38.6_4, C3; 24.5_8, C3Me; 24.8_7, C4; 137.6_0, Clipso C; 125.5_0, Clortho C; 128.3_7, Clmeta C; 127.9_4, Clpara C; 146.4_5, C3ipso C; 126.0_4, C3ortho C; 128.3_1, C3meta C; 126.3_8, C3para C.

Reaction of trans-1-d-1,3-diphenyl-1,2-epoxy-3-methylbutane(190a) with BF_3-etherate and lithium aluminium hydride

BF_3-etherate(0.25ml) was added to a solution of trans-1-d-1,3-diphenyl-1,2-epoxy-3-methylbutane(190a)(0.14g) in benzene(15ml) and the resulting mixture was stirred for 5 min. The crude reaction product, isolated as above, was taken up in dry ether and added to a stirred suspension of lithium aluminium hydride(0.005g) in dry ether. The mixture was heated under reflux for 0.5hr. The product, isolated as above, was absorbed onto alumina(13g). Elution with

light petroleum-ether(20:1) gave 1R*,2R*-1-d-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(192a)(0.035g) (Found: M^+, 149.0931 and 136.0812. $C_{19}H_{23}DO_2$ requires M^+, 238.1838; $M^+-C_9H_{10}DO$ requires 149.0966; $M^+-C_{10}H_{13}O$ requires 136.0872). $\nu_{max}(CCl_4)$ 1060, 3550cm^{-1}. ^{1}H n.m.r. δ 1.03, J 7Hz, $OCH_2\underline{Me}$; 1.35, C3Me; 1.40, $C4H_3$; 3.12, Wh/2 18Hz, $O\underline{CH_2}Me$; 3.64, Wh/2 6Hz, H2; 7.19, Wh/2 13Hz, ArH's. ^{13}C n.m.r. δ 82.3_2, C2; 42.7_5, C3; 22.5_0, C3Me; 27.1_5, C4; 15.1_8, $OCH_2\underline{Me}$; 63.9_4, $O\underline{CH_2}Me$; 141.5_0, Clipso C; 126.5_6, Clortho C; 128.2_6, Clmeta C; 127.4_3, Clpara C; 147.1_6, C3ipso C; 126.6_4, C3ortho C; 128.1_4, C3meta C; 126.0_2, C3para C.

Further elution with light petroleum-ether(5:1) afforded 2-d-2,3-diphenyl-3-methylbutan-1-ol(191a)(0.092g) (Found: M^+, 241.1601. $C_{17}H_{19}DO$ requires M^+, 241.1576). $\nu_{max}(CCl_4)$ 3625cm^{-1}. ^{1}H n.m.r. δ 1.20, C3Me, OH; 1.28, $C4H_3$; 3.68, J 12Hz, H1; 3.84, J 12Hz, H1'; 7.19, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 62.6_4, C2; 40.0_7, C3; 24.0_1, C3Me; 28.9_9, C4; 139.1_4, C2ipso C; 130.1_0, C2ortho C; 127.9_8, C2meta C; 126.9_0, C2para C; 148.0_9, C3ipso C; 126.3_1, C3ortho C; 127.9_8, C3meta C; 125.9_2, C3para C.

Oxidation of 1R*,2R*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(189a)

Jones reagent was added dropwise to a stirred solution of 1R*,2R*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(189a) (0.46g) in acetone until an orange/brown colour persisted. The resulting mixture was stirred for 0.5hr and sodium bisulphite was added. The solution was decanted and the precipitate washed with light petroleum. The combined organic fractions were washed with saturated sodium bicarbonate and sodium chloride solutions and dried over anhydrous magnesium sulphate. Removal of the solvent gave 1,3-diphenyl-

1-ethanoxy-3-methylbutan-2-one(197)(0.45g) (Found: M^+, 135.0691 and 147.0784; C, 80.8; H, 8.1. $C_{19}H_{22}O_2$ requires M^+, 282.1618; C,80.8; H, 7.9%; $M^+-C_{10}H_{11}O$ requires 135.0809; M^+- requires 147.0809). ν_{max}(neat) 1098, 1715cm^{-1}. λ_{max} 217nm(ε27613), 253.5(2452), 259.5(2581), 265.5(2258). ^{1}H n.m.r. δ 1.00, J 7Hz, $OCH_2\underline{Me}$; 1.35, C3Me; 1.55, $C4H_3$; 3.19, 2.99, J 7Hz, $O\underline{CH_2}Me$; 4.76, H1; 7.15, Wh/2 2Hz, ArH's. ^{13}C n.m.r. δ 82.5_0, C1; 214.1_0, C2; 51.9_9, C3; 25.0_1, C3Me; 25.5_6, C4; 15.0_0, $OCH_2\underline{Me}$; 64.6_3, $O\underline{CH_2}Me$; 137.0_1, C1ipso C; 128.1_8, C1ortho C; 128.5_3, C1meta C; 128.1_8, C1para C; 142.8_1, C3ipso C; 126.9_4, C3ortho C; 128.5_3, C3meta C; 126.6_9, C3para C.

Acetylation of 1R*,2R*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(189a)

Acetic anhydride(1ml) was added to a solution of 1R*,2R*-diphenyl-1-ethanoxy-3-methylbutan-2-ol(189a)(0.024g) in dry pyridine(15ml) and the resulting mixture was heated under reflux for 2hr. After cooling, the reaction mixture was poured into an ether/water mixture. The ethereal layer was washed successively with dilute sulphuric acid, sodium bicarbonate solution and water, and dried over anhydrous magnesium sulphate. The solvent was removed and the oily residue absorbed onto alumina(13g). Elution with light petroleum-ether(20:1) afforded 1R*,2R*-1,3-diphenyl-1-ethanoxy-3-methylbutyl-2-acetate(198)(0.017g) (Found: M^+, 267.1712; C, 77.3; H, 8.3. $C_{21}H_{26}O_3$ requires 326.1880; C, 77.3; H, 8.0%; M^+-OAc requires 267.1747). $\nu_{max}(CCl_4)$ 1060, 1215, 1740cm^{-1}. ^{1}H n.m.r. δ 1.08, J 7Hz, $OCH_2\underline{Me}$; 1.24, C3Me; 1.56, $C4H_3$; 1.93, OCO$\underline{Me}$; 3.12, Wh/2 19Hz, $O\underline{CH_2}Me$; 4.01, J 2.5Hz, H1; 5.20, J 2.5Hz, H2; 7.25, Wh/2 15Hz, ArH's. ^{13}C n.m.r. δ 82.0_1, C1; 80.6_2, C2; 42.2_2, C3; 22.8_9, C3$\underline{Me}$;

28.3_8, C4; 20.6_9, OCOMe; 15.2_5, $OCH_2\underline{Me}$; 64.6_3, $O\underline{CH_2}Me$; 170.1_4, $O\underline{C}OMe$; 138.0_5, Cl<u>ipso C</u>; 126.5_3, Cl<u>ortho C</u>; 128.0_4, Cl<u>meta C</u>; 127.4_8, Cl<u>para C</u>; 146.6_0, C3<u>ipso C</u>; 126.8_8, C3<u>ortho C</u>; 128.2_8, C3<u>meta C</u>; 126.3_4, C3<u>para C</u>.

<u>Reaction of trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a) with sodium ethoxide in ethanol</u>

Sodium(1g) was added to dry ethanol(50ml) and the mixture was stirred at room temperature until the reaction was complete. A solution of <u>trans</u>-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a)(0.5g) in dry ethanol was added to the sodium ethoxide solution and the resulting mixture was heated under reflux for 60hr. After cooling, the reaction mixture was poured into an ether/water mixture(1:1). The ethereal layer was separated and dried over magnesium sulphate. The solvent was removed and the residue absorbed onto alumina(80g). Elution with light petroleum-ether(50:1) gave unreacted <u>trans</u>-1,3-diphenyl-1,2-epoxy-3-methylbutane (89a)(0.36g) ^{1}H n.m.r. δ 1.32, C3Me; 1.41, $C4H_3$; 3.02, J 2Hz, H2; 3.73, J 2Hz, H1; 7.32, Wh/2 2Hz, ArH's.

Further elution with light petroleum-ether(10:1) afforded 1R*,2S*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(199) (0.13g) (Found: M^+, 136.0823 and 148.0838; C, 80.0; H, 8.9. $C_{19}H_{24}O_2$requires M^+, 284.1776; C, 80.2; H, 8.5%; $M^+-C_{10}H_{12}O$ requires 136.0887; $M^+-C_9H_{12}O$ requires 148.0887). $\nu_{max}(CCl_4)$ 1100, 3610cm^{-1}. ^{1}H n.m.r. δ 1.00, J 7Hz, $OCH_2\underline{Me}$; 1.30, C3Me; 1.43, $C4H_3$, OH; 3.07, Wh/2 15Hz, $O\underline{CH_2}Me$; 3.86, J 7Hz, H2; 3.92, J 7Hz, H1; 7.25, Wh/2 2Hz, ArH's. ^{13}C n.m.r. δ 80.7_0, C1; 83.1_0, C2; 42.0_3, C3; 25.0_0, C3Me; 25.6_4, C4; 15.1_4, $OCH_2\underline{Me}$; 63.6_7, $O\underline{CH_2}Me$; 140.0_3, Cl<u>ipso C</u>; 127.8_7, Cl<u>ortho C</u>; 128.1_2, Cl<u>meta C</u>; 127.8_7, Cl<u>para C</u>; 147.3_1, C3<u>ipso C</u>;

126.7_6, C3ortho C; 128.3_1, C3meta C; 125.8_7, C3para C.

Oxidation of 1R*,2S*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(199)

Jones reagent was added dropwise to a stirred solution of 1R*,2S*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(199)(0.03g) until an orange/brown colour persisted. The resulting mixture was stirred for 15 min. The product, isolated as above, was 1,3-diphenyl-1-ethanoxy-3-methylbutan-2-one(197) identified by comparison with an authentic sample. $\nu_{max}(CCl_4)$ 1715cm^{-1}. λ_{max} 217nm(ε27613), 253.3(2452), 259.5(2581), 265.5(2258). ^1H n.m.r. δ 1.00, J 7Hz, $OCH_2\underline{Me}$; 1.35, C3Me; 1.55, $C4H_3$; 3.09, J 7Hz, $O\underline{CH_2}Me$; 4.76, H1; 7.15, Wh/2 2Hz, ArH's.

Acetylation of 1R*,2S*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(199)

Acetic acid(2ml) was added to a solution of 1R*,2S*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(199)(0.045g) in dry pyridine and the resulting mixture was heated under reflux for 2hr. After cooling, the mixture was poured into an ether/water mixture. The product, isolated as above, was 1R*,2S*-1,3-diphenyl-1-ethanoxy-3-methylbutyl-2-acetate (200)(0.039g) (Found: M^+, 267.1729; C, 77.5; H, 8.2. $C_{21}H_{26}O_3$ requires M^+, 326.1880; C, 77.3; H, 8.0%; M^+-OAc requires 267.1747). $\nu_{max}(CCl_4)$ 1100, 1220, 1740cm^{-1}. ^1H n.m.r. δ 0.93, J 7Hz, $OCH_2\underline{Me}$; 1.36, C3Me; 1.50, $C4H_3$; 1.55, $OCO\underline{Me}$; 3.00, Wh/2 18Hz, $O\underline{CH_2}Me$; 3.97, J 8Hz, H1; 5.27, J 8Hz, H2; 7.36, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 82.0_2, C1; 80.6_2, C2; 41.6_2, C3; 25.5_1, C3Me; 26.2_4, C4; 15.0_6, $OCH_2\underline{Me}$; 20.3_2, $OCO\underline{Me}$; 63.9_6, $O\underline{CH_2}Me$; 169.3_0, $O\underline{C}OMe$; 139.7_6, C1ipso C; 127.7_9, C1ortho C; 127.7_9, C1meta C; 126.6_2, C1para C; 146.2_9, C3ipso C; 126.9_4, C3ortho C; 127.9_1, C3meta C;

126.0$_3$, C3para C.

Reaction of trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a) with boron trifluoride etherate in diethyl ether

BF_3-etherate(0.5ml) was added to a solution of trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a)(0.26g) in dry ether(25ml) and the resulting mixture was stirred at room temperature for 24hr. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum afforded 2,3-diphenyl-1-ethanoxy-3-methylbut-1-ene(207a) (0.06g). The E- and Z- isomers were detected in a ratio of 5:1 and insuffient of the minor isomer, ^{1}H n.m.r. δ 1.03, J 7Hz, OCH_2Me; 1.46, C3Me, $C4H_3$; 3.70, 3.48, J 7Hz, OCH_2Me; 5.83, H1; 7.20, Wh/2 12Hz, ArH's, could be isolated for full spectral analysis.

2,3-Diphenyl-1-ethanoxy-3-methylbut-1-ene(207a)

(Found: M^+, 147.0441 and 119.0873; C, 85.4; H, 8.3. $C_{19}H_{22}O$ requires M^+, 266.1669; C, 85.7; H, 8.3%; $M^+-C_{10}H_{11}O$ requires 119.0860; $M^+-C_9H_{11}$ requires 147.0809). $\nu_{max}(CCl_4)$ 1110, 1645cm^{-1}. ^{1}H n.m.r. δ 1.12, J 7Hz, OCH_2Me; 1.35, C3Me, $C4H_3$; 3.74, 3.56, J 7Hz, OCH_2Me; 6.03, H1; 6.90, Wh/2 21Hz, ArH's. ^{13}C n.m.r. δ 142.5$_2$, C1; 128.3$_9$, C2; 41.6$_0$, C3; 29.2$_8$, C3Me, C4; 15.2$_3$, OCH_2Me; 67.7$_2$, OCH_2Me; 138.0$_3$, C1ipso C; 130.0$_3$, C1ortho C; 127.2$_9$, C1meta C; 126.0$_2$, C1para C; 148.4$_8$, C3ipso C; 126.7$_4$, C3ortho C; 127.9$_2$, C3meta C; 125.6$_7$, C3para C.

Further elution with light petroleum-ether(50:1) gave 1,3-diphenyl-3-methylbutan-2-one(139a)(0.02g) ^{1}H n.m.r. δ 1.50, C3Me, $C4H_3$; 3.48, $C1H_2$; 7.10, Wh/2 5Hz, ArH's and 2,3-diphenyl-3-methylbutanal(140a)(0.07g) ^{1}H n.m.r. δ 1.40, C3Me; 1.45, $C4H_3$; 3.72, J 3Hz, H2; 7.08, Wh/2 3Hz, ArH's, 9.79, J 3Hz, H1. Elution with light petroleum-ether(20;1)

gave 1R*,2R*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(189a) (0.05g) ^{1}H n.m.r. δ 1.03, J 7Hz, $OCH_2\underline{Me}$; 1.28, OH; 1.35, C3Me; 1.40, $C4H_3$; 3.15, Wh/2 17Hz, $O\underline{CH_2}Me$; 3.64, Wh/2 6Hz, H2; 3.90, J 2Hz, H1; 7.18, Wh/2 11Hz, ArH's.

Elution with ether afforded di-(1R*,2S*-1,3-diphenyl-2-hydroxyl-3-methylbutane)ether(208a)(0.01g) $\nu_{max}(CCl_4)$ 1071, 3570cm^{-1}. ^{1}H n.m.r. δ 1.32, C3Me; 1.41, $C4H_3$; 2.58, Wh/2 11Hz, OH; 4.03, J 3.5Hz, H1; 4.73, J 3.5Hz, H2; 7.17, Wh/2 10Hz, ArH's. ^{13}C n.m.r. δ 81.2_5, C1; 65.6_7, C2; 43.2_1, C3; 22.7_5, C3Me; 27.3_9, C4; 140.9_6, C1ipso C; 127.2_9, C1ortho C; 128.2_6, C1meta C; 128.0_3, C1para C; 146.1_8, C3ipso C; 126.5_6, C3ortho C; 128.3_9, C3meta C; 126.4_1, C3para C.

Reaction of 2,3-diphenyl-1-ethanoxy-3-methylbut-1-ene(207a) with dilute hydrochloric acid

A mixture of 2,3-diphenyl-1-ethanoxy-3-methylbut-1-ene(207a)(0.02g) and dilute hydrochloric acid(5%)(20ml) was heated under reflux for 0.5hr[120]. After cooling, the product was extracted with ether, washed with water and dried over anhydrous magnesium sulphate. The residue isolated on the removal of solvent was 2,3-diphenyl-3-methylbutanal(140a)(0.02g) which was identified by comparison with an authentic sample. $\nu_{max}(CCl_4)$ 1715, 2720cm^{-1}. ^{1}H n.m.r. δ 1.40, C3Me; 1.45, $C4H_3$; 3.27, J 3Hz, H2; 7.08, Wh/2 3Hz, ArH's; 9.79, J 3Hz, H1.

Oxidation of di-(1R*,2S*-1,3-diphenyl-2-hydroxyl-3-methylbutane)ether(208a)

Jones reagent was added to a stirred solution of di-(1R*,2S*-1,3-diphenyl-2-hydroxyl-3-methylbutane)ether(208a) (0.13g) in acetone until an orange/brown colour persisted.

The resulting mixture was stirred for 0.5hr and sodium bisulphite was added. The oily residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(50:1) gave di-(1,3-diphenyl-3-methylbutan-2-one)ether (210)(0.072g) $\nu_{max}(CCl_4)$ 1070, 1725cm^{-1}. λ_{max} 209.5(ε25257). ^{1}H n.m.r. δ 1.38, C3Me; 1.62, C4H$_3$; 5.27, H1; 7.18, Wh/2 8Hz, ArH's. ^{13}C n.m.r. δ 58.3$_3$, C1; 204.7$_9$, C2; 52.8$_9$, C3; 25.1$_1$, C3Me, C4; 136.0$_7$, C1ipso C; 128.3$_3$, C1ortho C; 128.3$_3$, C1meta C; 128.7$_0$, C1para C; 141.4$_6$, C3ipso C; 126.7$_4$, C3ortho C; 128.8$_2$, C3meta C; 127.4$_8$, C3para C.

Acetylation of di-(1R*,2S*-1,3-diphenyl-2-hydroxyl-3-methyl-butane)ether(208a)

Acetic anhydride(2ml) was added to a solution of di-(1R*,2S*-1,3-diphenyl-2-hydroxyl-3-methylbutane)ether (208a)(0.12g) in dry pyridine(5ml) and the resulting mixture was heated under reflux for 2hr. After cooling, the reaction mixture was poured into an ether/water mixture(1:1). The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(50:1) afforded di-(1R*,2S*-1,3-diphenyl-3-methylbutyl-2-acetate)ether(212)(0.081g) $\nu_{max}(CCl_4)$ 1080, 1210, 1745cm^{-1}. ^{1}H n.m.r. δ 1.17, C3Me; 1.37, C4H$_3$; 2.12, OCOMe; 4.72, J 7.5Hz, H1; 5.64, J 7.5Hz, H2; 7.17, Wh/2 11Hz, ArH's. ^{13}C n.m.r. δ 63.4$_6$, C1; 81.0$_3$, C2; 42.4$_2$, C3; 23.9$_1$, C3Me; 27.5$_2$, C4; 20.7$_4$, OCOMe; 170.2$_0$, 169.2$_3$, OCOMe; 139.0$_9$, C1ipso C; 127.7$_9$, C1ortho C; 128.1$_6$, C1meta C; 127.7$_9$, C1para C; 145.1$_2$, C3ipso C; 126.5$_7$, C3ortho C; 128.2$_9$, C3meta C; 126.3$_8$, C3para C.

1R*,2S*-1,3-Diphenyl-3-methylbutane-1,2-diol(213)

Perchloric acid(0.5ml) was added to a solution of trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a)(0.354g) in tetrahydrofuran(35ml) and water(35ml) and the resulting mixture was stirred at room temperature for 6hr[121]. The reaction mixture was diluted with water(100ml) and the product was extracted with ether. The combined ether fractions were dried over magnesium sulphate and filtered. The residue crystallised on the removal of solvent. Recrystallisation from chloroform/light petroleum afforded 1R*,2S*-1,3-diphenyl-3-methylbutane-1,2-diol(213)(0.23g, m.p. 125-126°C) (Found: M^+, 238.1377. $C_{17}H_{20}O_2$requires M^+, 256.1462; M^+-H_2O requires 238.1357). $\nu_{max}(CCl_4)$ 3590cm^{-1}. ^1H n.m.r. δ 1.43, C3Me, $C4H_3$; 2.27, Wh/2 10Hz, OH; 3.75, Wh/2 5Hz, H2; 4.58, Wh/2 5Hz, H1; 7.23, Wh/2 13Hz, ArH's. ^{13}C n.m.r. δ 81.9_7, C1; 71.4_7, C2; 42.5_6, C3; 23.6_9, C3Me; 25.7_2, C4; 143.7_3, C1ipso C; 125.7_6, C1ortho C; 128.5_0, C1meta C; 127.3_7, C1para C; 146.4_6, C3ipso C; 126.6_4, C3ortho C; 128.3_5, C3meta C; 126.4_5, C3para C.

Reaction of trans-1,3-diphenyl-1,2-epoxy-3-methylbutane (89a) and 1R*,2S*-1,3-diphenyl-3-methylbutane-1,2-diol(213) with BF_3-etherate in ether

BF_3-etherate(0.25ml) was added to a solution of trans-1,3-diphenyl-1,2-epoxy-3-methylbutane(89a)(0.040g) and 1,3-diphenyl-3-methylbutane-1,2-diol(213)(0.035g) in dry ether(15ml) and the resulting mixture was stirred for 24hr. The oily residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether (50:1) gave 1,3-diphenyl-3-methylbutan-2-one(139a)(0.013g) ^1H n.m.r. δ 1.50, C3Me, $C4H_3$; 3.48, $C1H_2$; 7.10, Wh/2 5Hz, ArH's and 2,3-diphenyl-3-methylbutanal(140a)(0.017g)

^{1}H n.m.r. δ 1.40, C3Me; 1.45, C4H$_3$; 3.72, J 3Hz, H2; 7.08, Wh/2 3Hz, ArH's; 9.79, J 3Hz, H1. Further elution with light petroleum-ether(20:1) afforded 1R*,2R*-1,3-diphenyl-1-ethanoxy-3-methylbutan-2-ol(189a)(0.014g) ^{1}H n.m.r. δ 1.03, J 7Hz, OCH$_2$Me; 1.28, OH; 1.35, C3Me; 1.40, C4H$_3$; 3.15, Wh/2 17Hz, OCH$_2$Me; 3.64, Wh/2 6Hz, H2; 3.90, J 2Hz, H1; 7.18, Wh/2 11Hz, ArH's.

Reaction of trans-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b) with BF_3-etherate in benzene

BF_3-etherate(0.25ml) was added to a solution of trans-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b)(0.07g) in benzene(10ml) and the resulting mixture was stirred for 2 min. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(20:1) gave 2-(4'-methoxyphenyl)-3-methyl-3-phenylbutanal(140b)(0.036g) (Found: M^+, 268.1498. $C_{18}H_{20}O_2$ requires M^+, 268.1462). $\nu_{max}(CCl_4)$ 1720, 2720cm^{-1}. ^{1}H n.m.r. δ 1.35, C3Me; 1.42, C4H$_3$; 3.65, J 3.5Hz, H2; 3.75, ArOMe; 6.80, Wh/2 2Hz, C2ArH's; 7.25, Wh/2 2Hz, C3ArH's; 9.70, J 3.5Hz, H1. ^{13}C n.m.r. δ 190.3_1, C1; 67.9_3, C2; 41.1_9, C3; 25.6_8, C3Me; 27.7_6, C4; 55.1_6, ArOMe; 126.4_5, C2ipso C; 131.6_5, C2ortho C; 113.5_6, C2meta C; 158.9_2, C2para C; 146.3_2, C3ipso C; 126.6_9, C3ortho C; 128.1_1, C3meta C; 126.3_1, C3para C.

Further elution with light petroleum-ether(10:1) afforded 1R*,2R*-1-ethanoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-2-ol(189b)(0.024g)(Found: M^+, 314.1841; C, 76.4; H, 8.5. $C_{20}H_{26}O_3$ requires M^+, 314.1880; C, 76.4; H, 8.3%). $\nu_{max}(CCl_4)$ 1085, 1095, 3600cm^{-1}. ^{1}H n.m.r. δ 1.03, J 7Hz, OCH$_2$Me; 1.30, C3Me; 1.39, C4H$_3$; 3.10, Wh/2 16Hz, OCH$_2$Me; 3.68, J 3Hz, H2; 3.75, ArOMe; 3.91, J 3Hz, H1;

7.02, Wh/2 32Hz, ArH's. ^{13}C n.m.r. δ 79.0$_5$, C1; 82.4$_2$, C2; 42.6$_2$, C3; 22.8$_0$, C3Me; 27.1$_5$, C4; 15.1$_8$, OCH_2Me; 63.7$_1$, OCH_2Me; 55.1$_9$, ArOMe; 133.5$_4$, C1ipso C; 127.9$_2$, C1ortho C; 113.7$_1$, C1meta C; 159.0$_7$, C1para C; 149.1$_1$, C3ipso C; 126.7$_1$, C3ortho C; 128.1$_0$, C3meta C; 125.9$_8$, C3para C.

Reaction of 2-(4'-methoxyphenyl)-3-methyl-3-phenylbutanal (140b) with lithium aluminium hydride

BF_3-etherate(0.25ml) was added to a solution of trans-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b)(0.08g) in benzene(10ml) and the resulting mixture was stirred for 2 min. The residue, isolated as above, was taken up in dry ether and added to a stirred suspension of lithium aluminium hydride in dry ether. The resulting mixture was heated under reflux for 0.5hr. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(5:1) gave 1R*,2R*-1-ethanoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-2-ol(189b)(0.028g) ^{1}H n.m.r. δ 1.03, J 7Hz, OCH_2Me; 1.30, C3Me; 1.39, C4H$_3$; 3.10, Wh/2 16Hz, OCH_2Me; 3.68, J 3Hz, H2; 3.75, ArOMe; 3.91, J 3Hz, H1; 7.02, Wh/2 32Hz, ArH's. Further elution with ether afforded 2-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-1-ol(153b)(0.025g) (Found: M^+, 270.1477; C, 79.6, H, 8.4. $C_{18}H_{22}O_2$ requires M^+, 270.1618; C, 79.9; H, 8.2%). $\nu_{max}(CCl_4)$ 3600cm^{-1}. ^{1}H n.m.r. δ 1.20, C3Me; 1.27, C4H$_3$; 1.38, OH; 3.02, J 5Hz, J 10Hz, H2; 3.78, ArOMe; 3.72, Wh/2 13Hz, C1H$_2$; 6.90, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 62.7$_8$, C1; 58.7$_7$, C2; 40.2$_7$, C3; 24.1$_1$, C3Me; 28.9$_9$, C4; 55.2$_0$, ArOMe; n.o., C2ipso C; 131.0$_6$, C2ortho C; 113.5$_4$, C2meta C; n.o., C2para C; n.o., C3ipso C; 126.3$_9$, C3ortho C; 128.0$_6$, C3meta C; 125.9$_2$, C3para C.

trans-1-d-1,2-Epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(190b)

m-Chloroperbenzoic acid(0.1g) was added to a solution of trans-1-d-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(110b)(0.26g) in ether and the resulting mixture was stirred at 4°C for 4 days. The residue, isolated as above, was absorbed onto an alumina dry column(13g). Light petroleum-ether(20:1) was allowed to percolate through the column. Elution of the segment c. Rf 1 to 0.55 with ether afforded trans-1-d-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(110b)(0.05g) ^{1}H n.m.r. δ 1.45, C3Me, $C4H_3$; 3.62, ArOMe; 6.22, H2; 7.00, Wh/2 32Hz, ArH's. Elution of the segment c. Rf 0.55 to 0.05 with ether gave trans-1-d-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(190b) (0.22g) (Found: M^+, 269.1534. $C_{18}H_{19}DO_2$ requires 269.1525). $\nu_{max}(CCl_4)$ 1235cm^{-1}. ^{1}H n.m.r. δ 1.32, C3Me; 1.40, $C4H_3$; 3.03, H2; 3.75, ArOMe; 7.10, Wh/2 30Hz, ArH's. ^{13}C n.m.r. δ 69.6_2, C2; 38.6_1, C3; 24.6_0, C3Me; 24.9_0, C4; 55.2_0, ArOMe; 129.5_3, Clipso C; 126.8_9, Clortho C; 113.9_6, Clmeta C; 159.6_0, Clpara C; n.o., C3ipso C; 126.0_6, C3ortho C; 128.3_1, C3meta C; 126.3_5, C3para C.

Reaction of trans-1-d-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(190b) with BF_3-etherate and lithium aluminium hydride

BF_3-etherate(0.25ml) was added to a solution of trans-1-d-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(190b)(0.12g) in benzene(12ml) and the resulting mixture was stirred for 2 min. The residue, isolated as above, was taken up in dry ether and added to a stirred suspension of lithium aluminium hydride in dry ether. The residue, isolated as above, was absorbed onto alumina(13g).

Elution with light petroleum-ether(20:1) gave 1R*,2R*-1-d-1-ethanoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-2-ol (192b)(0.019g) (Found: M^+, 315.1868. $C_{20}H_{25}DO_3$ requires M^+, 315.1943). $\nu_{max}(CCl_4)$ 1080, 3550cm^{-1}. ^{1}H n.m.r. δ 1.01, J 7Hz, $OCH_2\underline{Me}$; 1.30, C3Me; 1.38, $C4H_3$, OH; 3.12, Wh/2 23Hz, $O\underline{CH_2}Me$; 3.65, Wh/2 6Hz, H2; 3.72, ArOMe; 6.94, Wh/2 32Hz, ArH's. ^{13}C n.m.r. δ 82.2_9, C2; 42.5_7, C3; 22.7_9, C3Me; 27.1_1, C4; 55.2_2, ArOMe; 15.1_8, $OCH_2\underline{Me}$; 63.6_2, $O\underline{CH_2}Me$; n.o., Clipso C; 127.8_8, Clortho C; 113.6_7, Clmeta C; 159.0_3, Clpara C; n.o., C3ipso C; 126.6_6, C3ortho C; 128.0_7, C3meta C; 125.9_2, C3para C.

Elution with ether afforded 2-d-2-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-1-ol(191b)(0.012g) (Found: M^+, 271.1748. $C_{18}H_{21}DO_2$ requires M^+, 271.1681). $\nu_{max}(CCl_4)$ 3600cm^{-1}. ^{1}H n.m.r. δ 1.20, C3Me; 1.27, $C4H_3$; 3.72, ClH_2; 3.77, ArOMe; 7.02, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 62.7_0, C2; n.o., C3; 24.0_3, C3Me; 28.9_5, C4; 55.1_7, ArOMe; n.o., C2ipso C; 131.0_0, C2ortho C; 113.5_1, C2meta C; 158.5_8, C2para C; 126.3_2, C3ortho C; 128.0_2, C3meta C; 125.9_0, C3para C.

Reaction of trans-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b) with BF_3-etherate in ether

BF_3-etherate(0.5ml) was added to a solution of trans-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b)(0.44g) in dry ether(50ml) and the resulting mixture was stirred at room temperature for 25hr. The residue, isolated as above, was absorbed onto alumina(80g). Elution with light petroleum-ether(50:1) afforded trans-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b) (0.012g) ^{1}H n.m.r. δ 1.40, C3Me; 1.50, $C4H_3$; 3.04, J 2Hz, H2; 3.72, J 2Hz, H1; 3.77, ArOMe; 7.10, Wh/2 31Hz, ArH's,

2-(4'-methoxyphenyl)-3-methyl-3-phenylbutanal(140b)(0.10g) ^{1}H n.m.r. δ 1.35, C3Me; 1.42, C4H$_3$; 3.65, J 3.5Hz, H2; 3.75, ArOMe; 6.80, C2ArH's; 7.25, C3ArH's; 9.70, J 3.5Hz, H1 and 1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-2-one(139b) (0.107g) ^{1}H n.m.r. δ 1.50, C3Me, C4H$_3$; 3.42, C1H$_2$; 3.72, ArOMe; 6.82, C1ArH's; 7.20, Wh/2 17Hz, C3ArH's. Further elution with light petroleum-ether(10:1) afforded 1R*,2R*-1-ethanoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-2-ol (189b)(0.073g) ^{1}H n.m.r. δ 1.03, J 7Hz, OCH$_2$Me; 1.30, C3Me; 1.39, C4H$_3$; 3.10, Wh/2 16Hz, OCH$_2$Me; 3.68, J 3Hz, H2; 3.75, ArOMe; 3.91, J 3Hz, H1; 7.02, Wh/2 32Hz, ArH's.

1-Ethanoxy-2-(4'-methoxyphenyl)-3-methyl-3-phenyl-but-1-ene(207b)(c. 0.004g) was detected in the ^{1}H n.m.r. spectrum of the crude reaction product, δ 6.20, H1, however insuffient was formed to enable full spectroscopic analysis.

Reaction of trans-1,2-epoxy-1-(4'-methylphenyl)-3-methyl-3-phenylbutane(89c) with BF$_3$-etherate

BF$_3$-etherate(0.25ml) was added to a solution of trans-1,2-epoxy-1-(4'-methylphenyl)-3-methyl-3-phenyl-butane(89c)(0.15g) in benzene(15ml) and the resulting mixture was stirred for 2 min. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(50:1) gave 2-(4'-methylphenyl)-3-methyl-3-phenylbutanal(140c)(0.074g) ν_{max}(CCl_4) 1720, 2720cm^{-1}. ^{1}H n.m.r. δ 1.37, C3Me; 1.42, C4H$_3$; 2.33, ArMe; 3.70, J 3Hz, H2; 7.10, Wh/2 2Hz, ArH's; 9.81, J 3Hz, H1. ^{13}C n.m.r. δ 202.0$_3$, C1; 68.3$_9$, C2; 41.1$_8$, C3; 25.6$_7$, C3Me; 27.9$_0$, C4; 21.0$_5$, ArMe; 131.4$_7$, C2ipso C; 130.5$_4$, C2ortho C; 128.8$_3$, C2meta C; 137.0$_9$, C2para C; 145.0, C3ipso C; 126.1$_7$, C3ortho C; 128.1$_7$, C3meta C; 126.3$_5$, C3para C.

Further elution with light petroleum-ether(20:1) afforded 1R*,2R*-1-ethanoxy-1-(4'-methylphenyl)-3-methyl-3-phenylbutan-2-ol(189c)(0.049g) (Found: M^+, 149.0955. $C_{20}H_{26}O_2$ requires M^+, 298.1931; ½(M^+), 149.0966). $\nu_{max}(CCl_4)$ 1067, 1073, 1094, 1117, 3550cm^{-1}. ^{1}H n.m.r. δ 1.03, J 7Hz, $OCH_2\underline{Me}$; 1.32, C3Me; 1.40, $C4H_3$, OH; 2.38, ArMe; 3.13, Wh/2 18Hz, $O\underline{CH_2}Me$; 3.69, Wh/2 10Hz, H2; 3.92, J 2.5Hz, H1; 7.02, Wh/2 3Hz, ClArH's; 7.35, Wh/2 5Hz, C3ArH's. ^{13}C n.m.r. δ 79.1_4, C1; 82.3_7, C2; 42.6_7, C3; 22.7_0, C3Me; 27.1_0, C4; 21.0_8, ArMe; 15.1_6, OCH_2Me; 63.8_1, $O\underline{CH_2}Me$; 138.4_7, C1ipso C; 126.6_2, C1ortho C; 128.9_1, C1meta C; 137.0_5, C1para C; 147.1_6, C3ipso C; 126.6_2, C3ortho C; 128.0_7, C3meta C; 125.9_2, C3para C.

Reaction of 2-(4'-methylphenyl)-3-methyl-3-phenylbutanal (140c) with lithium aluminium hydride

BF_3-etherate(0.5ml) was added to a solution of trans-1,2-epoxy-1-(4'-methylphenyl)-3-methyl-3-phenylbutane(89c)(0.19g) in benzene(20ml) and the resulting mixture was stirred for 2 min. The residue, isolated as above, was absorbed onto alumina(80g). Elution with light petroleum-ether(50:1) afforded 2-(4'-methylphenyl)-3-methyl-3-phenylbutanal(140c)(0.086g) ^{1}H n.m.r. δ 1.37, C3Me; 1.42, $C4H_3$; 2.33, ArMe; 3.70, J 3Hz, H2; 7.10, Wh/2 2Hz, ArH's; 9.81, J 3Hz, H1. The aldehyde(140c) was taken up in dry ether and added to a stirred suspension of lithium aluminium hydride in dry ether. The resulting mixture was heated under reflux for 0.5hr. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(5:1) afforded 2-(4'-methylphenyl)-3-methyl-3-phenylbutan-1-ol(153c)(0.056g) $\nu_{max}(CCl_4)$ 3600cm^{-1}. ^{1}H n.m.r. δ 1.20, C3Me; 1.28, $C4H_3$; 1.42, OH;

2.32, ArMe; 3.07, J 4Hz, J 10Hz, H2; 3.72, Wh/2 14Hz, ClH_2; 7.01, Wh/2 3Hz, C2ArH's; 7.27, Wh/2 4Hz, C3ArH's. ^{13}C n.m.r. δ 62.7_4, C1; 59.1_2, C2; 40.1_8, C3; 23.9_5, C3Me; 29.1_4, C4; 21.0_3, ArMe; 136.4_6, C2ipso C; 130.0_2, C2ortho C; 128.7_9, C2meta C; 135.8_8, C2para C; 148.1_9, C3ipso C; 126.3_5, C3ortho C; 128.0_6, C3meta C; 125.9_1, C3para C.

Reaction of trans-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89d) with BF_3-etherate in benzene

BF_3-etherate(0.25ml) was added to a solution of trans-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89d)(0.10g) in benzene(10ml) and the resulting mixture was stirred for 2 min. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(50:1) gave 2-(4'-chlorophenyl)-3-methyl-3-phenylbutanal(140d)(0.033g) $\nu_{max}(CCl_4)$ 1725, 2720cm^{-1}. ^1H n.m.r. δ 1.42, C3Me, $C4H_3$; 3.72, J 3Hz, H2; 7.07, Wh/2 3Hz, ArH's; 9.73, J 3Hz, H1. ^{13}C n.m.r. δ 201.4_9, C1; 67.9_8, C2; 41.3_7, C3; 25.8_1, C3Me; 27.5_7, C4; 133.0_5, C2ipso C; 131.8_4, C2ortho C; 129.2_6, C2meta C; 133.5_0, C2para C; 145.7_5, C3ipso C; 126.5_7, C3ortho C; 128.2_7, C3meta C; 126.4_6, C3para C.

Elution with light petroleum-ether(10:1) afforded 1R*,2R*-1-(4'-chlorophenyl)-1-ethanoxy-3-methyl-3-phenylbutan-2-ol(189d)(0.017g) (Found: C, 71.7; H, 7.6. $C_{19}H_{23}ClO_2$ requires C, 71.7; H, 7.3%). $\nu_{max}(CCl_4)$ 1070, 1090, 3600cm^{-1}. ^1H n.m.r. δ 1.02, J 7Hz, OCH_2Me; 1.30, C3Me; 1.38, $C4H_3$; 1.52, OH; 3.04, Wh/2 20Hz, OCH_2Me; 3.60, J 3Hz, J 9Hz, H2; 3.87, J 3Hz, H1; 7.07, Wh/2 6Hz, ArH's. ^{13}C n.m.r. δ 78.6_2, C1; 82.3_2, C2; 42.7_3, C3; 22.0_8, C3Me; 27.3_9, C4; 15.1_4, OCH_2Me; 64.1_0, OCH_2Me; 140.0_5, C1ipso C; 128.3_7, C1ortho C; 128.1_7, C1meta C; 133.1_1, C1para C; 146.9_2, C3ipso C;

126.5$_6$, C3ortho C; 127.9$_3$, C3meta C; 126.0$_7$, C3para C.

Reaction of 2-(4'-chlorophenyl)-3-methyl-3-phenylbutanal (140d) with lithium aluminium hydride

BF_3-etherate(0.25ml) was added to a solution of trans-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89d)(0.14g) in benzene(15ml) and the resulting mixture was stirred for 5 min. The residue, isolated as above, was taken up in dry ether and added to a stirred suspension of lithium aluminium hydride(0.005g) in dry ether. The resulting mixture was heated under reflux for 0.5hr. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(10:1) gave 1R*,2R*-1-(4'-chlorophenyl)-1-ethanoxy-3-methyl-3-phenylbutan-2-ol(189d)(0.044g) ^{1}H n.m.r. δ 1.02, J 7Hz, $OCH_2\underline{Me}$; 1.30, C3Me; 1.38, $C4H_3$; 1.52, OH; 3.04, Wh/2 20Hz, $O\underline{CH_2}Me$; 3.60, J 3Hz, J 9Hz, H2; 3.87, J 3Hz, H1; 7.07, Wh/2 6Hz, ArH's.

Further elution with ether afforded 2-(4'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(153d)(0.065g) (Found: M^+, 274.1350. $C_{17}H_{19}ClO$ requires M^+, 274.1123). $\nu_{max}(CCl_4)$ 3625cm^{-1}. ^{1}H n.m.r. δ 1.08, OH; 1.20, C3Me; 1.28, $C4H_3$; 3.05, J 6Hz, J 9Hz, H2; 3.75, Wh/2 2Hz, ClH_2; 7.15, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 62.6$_1$, C1; 58.9$_4$, C2; 40.1$_4$, C3; 24.3$_7$, C3Me; 28.5$_9$, C4; 137.8$_4$, C2ipso C; 131.2$_9$, C2ortho C; 128.0$_8$, C2meta C; 132.6$_6$, C2para C; 147.6$_1$, C3ipso C; 126.2$_8$, C3ortho C; 128.0$_8$, C3meta C; 126.0$_8$, C3para C.

trans-1-d-1-(4'-Chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(190d)

m-Chloroperbenzoic acid(0.45g) was added to a

solution of trans-1-d-(4'-chlorophenyl)-3-methyl-3-phenyl-but-1-ene(110d)(0.8g) in ether and the resulting mixture was stirred at 4°C for 5 days. The residue, isolated as above, was absorbed onto alumina(80g). Elution with light petroleum gave trans-1-d-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(110d)(0.3g) ^{1}H n.m.r. δ 1.45, C3Me, C4H$_3$; 6.40, H2; 7.30, Wh/2 7Hz, ArH's. Further elution with light petroleum-ether afforded trans-1-d-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(190d)(0.5g) (Found: M$^+$, 273.0985. $C_{17}H_{16}ClDO$ requires M$^+$, 273.1029). ν_{max}(neat) 890, 1250cm^{-1}. ^{1}H n.m.r. δ 1.32, C3Me; 1.42, C4H$_3$; 2.97, H2; 7.23, Wh/2 8Hz, ArH's. ^{13}C n.m.r. δ 70.0_1, C2; 38.5_7, C3; 24.5_0, C3Me; 24.8_3, C4; 136.1_6, Clipso C; 126.8_0, Clortho C; 128.3_1, Clmeta C; 133.6_9, Clpara C; 146.1_9, C3ipso C; 125.9_7, C3ortho C; 128.6_0, C3meta C; 126.4_2, C3para C.

Reaction of trans-1-d-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(190d) with BF_3-etherate and lithium aluminium hydride

BF_3-etherate(0.5ml) was added to a solution of trans-1-d-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane (190d)(0.25g) in benzene(25ml) and the resulting mixture was stirred for 5 min. The residue, isolated as above, was taken up in dry ether and added to a stirred solution of lithium aluminium hydride in dry ether. The resulting mixture was heated under reflux for 0.5hr. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(20:1) gave 1R*,2R*-1-d-1-(4'-chlorophenyl)-1-ethanoxy-3-methyl-3-phenylbutane(192d)(0.048g) (Found: M$^+$, 149.0863 and 170.0457. $C_{19}H_{22}ClDO_2$ requires M$^+$, 319.1428; M$^+$-C_9H_9ClDO requires 149.0966; M$^+$-$C_{10}H_{13}O$ requires 170.0481). $\nu_{max}(CCl_4)$ 1080, 3570cm^{-1}. ^{1}H n.m.r. δ 1.04,

J 7Hz, OCH_2Me; 1.32, C3Me; 1.40, $C4H_3$; 3.05, Wh/2 11Hz, OCH_2Me; 3.60, J 8Hz, H2; 7.15, Wh/2 4Hz, ArH's. ^{13}C n.m.r. δ 82.2_6, C2; 42.7_1, C3; 22.1_0, C3Me; 27.3_8, C4; 15.1_6, OCH_2Me; 64.0_5, OCH_2Me; n.o., Clipso C; 128.4_0, Clortho C; 128.2_1, Clmeta C; n.o., Clpara C; n.o., C3ipso C; 126.5_5, C3ortho C; 127.9_6, C3meta C; 126.1_0, C3para C.

Further elution with ether afforded 2-d-2-(4'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(191d)(0.135g) (Found: M^+, 244.0051; C, 74.4; H(D), 7.3. $C_{17}H_{18}ClDO$ requires M^+, 275.1176; C, 74.2; H(D), 7.3%; M^+-CH_2OH requires 244.1002). ν_{max}(neat) 3380cm^{-1}. ^{1}H n.m.r. δ 1.20, C3Me, OH; 1.28, $C4H_3$; 3.73, J 11Hz, H1; 3.81, J 11Hz, H1'; 7.13, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 62.4_0, C1; 39.9_9, C3; 24.2_9, C3Me; 28.5_7, C4; n.o., C2ipso C; 131.2_5, C2ortho C; 128.0_4, C2meta C; 132.5_6, C2para C; n.o., C3ipso C; 126.2_6, C3ortho C; 128.0_4, C3meta C; 126.0_3, C3para C.

Reaction of trans-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89d) with BF_3-etherate in ether

BF_3-etherate(0.5ml) was added to a solution of trans-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane (89d)(0.25g) in dry ether(25ml) and the resulting mixture was stirred at room temperature for 24hr. The residue, isolated as above, was absorbed onto alumina(80g). Elution with light petroleum afforded 2-(4'-chlorophenyl)-1-ethanoxy-3-methyl-3-phenylbut-1-ene(207d)(0.06g). The two isomers were formed in a ratio of 5:1, however insufficient of the minor isomer, ^{1}H n.m.r. δ 1.20, J 7Hz, OCH_2Me; 1.43, C3Me, $C4H_3$; 3.49, 3.71, J 7Hz, OCH_2Me; 5.85, H1, 7.30, ArH's, could be isolated for full spectroscopic analysis.

2-(4'-Chlorophenyl)-1-ethanoxy-3-methyl-3-phenylbut-1-ene(207d) $\nu_{max}(CCl_4)$ 1115, 1650cm^{-1}. ^{1}H n.m.r.

δ 1.17, J 7Hz, OCH_2Me; 1.39, C3Me, $C4H_3$; 3.83, 3.61, J 7Hz, OCH_2Me; 6.20, H1; 6.97, Wh/2 42Hz, ArH's. ^{13}C n.m.r. δ 142.7_5, C1; 127.5_6, C2; 41.5_3, C3; 29.1_5, C3Me; 29.7_1, C4; 15.2_6, OCH_2Me; 67.8_7, OCH_2Me; 136.4_4, C2ipso C; 131.4_2, C2ortho C; 127.5_6, C2meta C; 131.9_1, C2para C; 148.1_1, C3ipso C; 126.6_4, C3ortho C; 128.0_4, C3meta C; 125.8_5, C3para C.

Further elution with light petroleum-ether(50:1) afforded trans-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89d)(0.01g) ^{1}H n.m.r. δ 1.25, C3Me; 1.35, $C4H_3$; 2.81, J 2Hz, H2; 3.55, J 2Hz, H1; 7.15, Wh/2 7Hz, ArH's, 1-(4'-chlorophenyl)-3-methyl-3-phenylbutanal(140d)(0.04g) ^{1}H n.m.r. δ 1.42, C3Me, $C4H_3$; 3.72, J 3Hz, H2; 7.07, Wh/2 3Hz, ArH's; 9.73, J 3Hz, H1 and 1-(4'-chlorophenyl)-3-methyl-3-phenylbutan-2-one(139d)(0.015g) ^{1}H n.m.r. δ 1.52, C3Me, $C4H_3$; 3.44, ClH_2; 7.02, Wh/2 6Hz, ArH's. Elution with light petroleum-ether(20:1) afforded 1R*,2R*-1-(4'-chlorophenyl)-1-ethanoxy-3-methyl-3-phenylbutan-2-ol(189d)(0.02g) ^{1}H n.m.r. δ 1.02, J 7Hz, OCH_2Me; 1.30, C3Me; 1.38, $C4H_3$; 1.52, OH; 3.04, Wh/2 20Hz, OCH_2Me; 3.60, J 3Hz, J 9Hz, H2; 3.87, J 3Hz, H1; 7.07, Wh/2 6Hz, ArH's.

Further elution afforded di-(1R*,2S*-1-(4'-chlorophenyl)-2-hydroxyl-3-methyl-3-phenylbutane)ether(208d)(0.02g) $\nu_{max}(CCl_4)$ 1090, 3600cm^{-1}. ^{1}H n.m.r. δ C3Me; 1.39, $C4H_3$; 2.53, Wh/2 11Hz, OH; 4.00, J 3.5Hz, H2; 4.67, J 3.5Hz, H1; 7.10, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 81.1_9, C1; 64.7_5, C2; 43.1_7, C3; 22.1_7, C3Me; 27.6_8, C4; 139.3_5, C1ipso C; 128.6_5, C1ortho C; 128.5_0, C1meta C; 133.9_5, C1para C; 145.9_5, C3ipso C; 126.3_7, C3ortho C; 128.3_8, C3meta C; 126.3_7, C3para C.

Reaction of trans-1-d-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(190d) with BF_3-etherate in ether

BF_3-etherate(0.5ml) was added to a solution of trans-1-d-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(190d)(0.1g) in dry ether and the resulting mixture was stirred for 24hr at room temperature. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum afforded 2-(4'-chlorophenyl)-1-ethanoxy-3-methyl-3-phenylbut-1-ene(207d)(0.025g) ^1H n.m.r. δ 1.17, J 7Hz, $OCH_2\underline{Me}$; 1.39, C3Me, $C4H_3$; 3.72, J 7Hz, $O\underline{CH_2}Me$; 6.20, H1; 6.97, Wh/2 42Hz, ArH's. Elution with light petroleum-ether(50:1) gave 1-d-1-(4'-chlorophenyl)-3-methyl-3-phenylbutan-2-one(d-139d)(0.009g) ^1H n.m.r. δ 1.52, C3Me, $C4H_3$; 3.44, H1; 7.02, Wh/2 6Hz, ArH's and 2-d-2-(4'-chlorophenyl)-3-methyl-3-phenylbutanal(193d)(0.023g) ^1H n.m.r. δ 1.35, C3Me, $C4H_3$; 7.17, Wh/2 3Hz, ArH's; 9.70, H1. Elution with light petroleum-ether(20:1) afforded 1R*,2R*-1-d-1-(4'-chlorophenyl)-1-ethanoxy-3-methyl-3-phenylbutan-2-ol(192d) (0.015g) ^1H n.m.r. δ 1.04, J 7Hz, $OCH_2\underline{Me}$; 1.32, C3Me, Oh; 1.40, $C4H_3$; 3.05, Wh/2 11Hz, $O\underline{CH_2}Me$; 3.60, J 8Hz, H2; 7.15, Wh/2 4Hz, ArH's and di-(1-d-1R*,2S*-1-(4'-chlorophenyl)-2-hydroxyl-3-methyl-3-phenylbutane)ether(d-208d)(0.01g) ^1H n.m.r. δ 1.30, C3Me; 1.39, $C4H_3$; 2.50, OH; 4.00, H1; 7.10, Wh/2 3Hz, ArH's.

Reaction of trans-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89e) with BF_3-etherate in benzene

BF_3-etherate(0.25ml) was added to a solution of trans-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89e)(0.06g) in benzene(10ml) and the resulting mixture was stirred for 2 min. The residue, isolated as above, was absorbed onto alumina(13g). Elution with

light petroleum-ether(100:1) afforded 2-(3'-chlorophenyl)-3-methyl-3-phenylbutanal(140e)(0.04g) $\nu_{max}(CCl_4)$ 1720, 2720cm^{-1}. ^{1}H n.m.r. δ 1.38, C3Me; 1.41, C4H$_3$; 3.68, J 3Hz, H2; 7.08, Wh/2 3Hz, ArH's; 9.68, J 3Hz, H1. ^{13}C n.m.r. δ 201.1$_2$, C1; 68.1$_3$, C2; 41.2$_9$, C3; 25.6$_5$, C3Me; 27.6$_4$, C4; 136.5$_5$, C2C$_1$; 130.5$_3$, C2C$_2$; 133.8$_1$, C2C$_3$; 127.7$_6$, C2C$_4$; 129.0$_6$, C2C$_5$; 128.6$_9$, C2C$_6$; 145.5$_2$, C3ipso C; 126.4$_7$, C3ortho C; 128.2$_4$, C3meta C; 126.3$_8$, C3para C.

Reaction of 2-(3'-chlorophenyl)-3-methyl-3-phenylbutanal (140e) with lithium aluminium hydride

BF_3-etherate(0.5ml) was added to a solution of trans-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89e) (0.12g) in benzene(12ml) ane the resulting mixture was stirred for 5 min. The residue, isolated as above, was taken up in dry ether and was added to a stirred suspension of lithium aluminium hydride in dry ether. The resulting mixture was heated under reflux for 0.5hr. The residue, isolated as above, was absorbed onto alumina(13g). Elution with ether afforded 2-(3'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(153e)(0.082g) (Found: M^+, 256.0097. $C_{17}H_{19}ClO$ requires M^+, 274.1124; M^+-H_2O requires 256.1019). ν_{max}(neat) 3380cm^{-1}. ^{1}H n.m.r. δ 1.20, C3Me; 1.23, OH; 1.25, C4H$_3$; 3.02, J 5Hz, J 10Hz, H2; 3.72, Wh/2 7Hz, C1H$_2$; 7.13, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 62.5$_1$, C1; 59.2$_5$, C2; 40.1$_1$, C3; 24.1$_9$, C3Me; 28.7$_4$, C4; 141.6$_7$, C2C$_1$; 130.0$_0$, C2C$_2$; 133.8$_1$, C2C$_3$; 126.9$_7$, C2C$_4$; 129.0$_7$, C2C$_5$; 128.2$_4$, C2C$_6$; 147.5$_7$, C3ipso C; 126.2$_4$, C3ortho C; 128.0$_9$, C3meta C; 126.0$_9$, C3para C.

trans-1-d-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(190e)

m-Chloroperbenzoic acid(0.2g) was added to a solution

of trans-1-d-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene (110e)(0.43g) in ether and the resulting mixture was stirred for 6 days at 4°C. The residue, isolated as above, was absorbed onto an alumina dry column(13g). Light petroleum-ether(100:1) was allowed to percolate through the column. Elution of the segment c. Rf 1 to 0.5 gave trans-1-d-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(110e)(0.15g) ^{1}H n.m.r. δ 1.47, C3Me, $C4H_3$; 6.35, H2; 7.15, Wh/2 12Hz, ArH's. Elution of the segment c. Rf 0.5 to 0.1 gave trans-1-d-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane (190e)(0.22g) $\nu_{max}(CCl_4)$ 880cm^{-1}. ^{1}H n.m.r. δ 1.25, C3Me; 1.35, $C4H_3$; 2.82, H2; 7.25, Wh/2 10Hz, ArH's. ^{13}C n.m.r. δ 70.0_8, C2; 38.6_2, C3; 24.5_6, C3Me; 24.8_5, C4; 139.8_7, ClC_1; 125.5_7, ClC_2; 134.5_7, ClC_3; 128.1_2, ClC_4; 129.7_3, ClC_5; 123.7_2, ClC_6; 146.0_8, C3ipso C; 126.0_2, C3ortho C; 128.3_6, C3meta C; 126.5_1, C3para C.

Reaction of trans-1-d-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(190e) with BF_3-etherate and lithium aluminium hydride

BF_3-etherate(0.5ml) was added to a solution of trans-1-d-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenyl butane(190e)(0.11g) in benzene(10ml) and the resulting mixture was stirred for 5 min. The residue, isolated as above, was taken up in dry ether and added to a stirred suspension of lithium aluminium hydride in dry ether. The resulting mixture was heated under reflux for 0.5hr. The residue, isolated as above, was absorbed onto alumina(13g). Elution with ether gave 2-d-2-(3'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(191e)(0.072g) (Found: M^+, 275.0109; C, 74.1; H(D), 7.1. $C_{17}H_{18}ClDO$ requires M^+, 275.1186; C, 74.2; H(D), 7.3%). $\nu_{max}(CCl_4)$ 3620cm^{-1}. ^{1}H n.m.r. δ 1.21, C3Me;

1.29, C4H_3, OH; 3.63, J 11Hz, H1; 3.87, J 11Hz, H1'; 7.13, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 62.5$_0$, C2; 40.0$_6$, C3; 24.1$_8$, C3Me; 28.7$_6$, C4; 141.6$_4$, C2$\underline{C}_1$; 130.0$_2$, C2$\underline{C}_2$; 133.8$_4$, C2$\underline{C}_3$; 127.0$_0$, C2$\underline{C}_4$; 129.0$_9$, C2$\underline{C}_5$; 128.2$_1$, C2$\underline{C}_6$; 147.6$_0$, C3ipso C; 126.2$_6$, C3ortho C; 128.1$_2$, C3meta C; 126.1$_2$, C3para C.

Reaction of trans-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89e) with BF_3-etherate in ether

BF_3-etherate(0.5ml) was added to a solution of trans-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane (89e)(0.23g) in dry ether(25ml) and the resulting mixture was stirred at room temperature for 24hr. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum afforded 2-(3'-chlorophenyl)-1-ethanoxy-3-methyl-3-phenylbut-1-ene(207e)(0.011g) $\nu_{max}(CCl_4)$ 1110, 1650cm^{-1}. ^{1}H n.m.r. δ 1.15, J 7Hz, OCH$_2$Me; 1.39, C3Me, C4H_3; 3.78, J 7Hz, OCH$_2$Me; 6.22, H1; 6.97, Wh/2 7Hz, ArH's. ^{13}C n.m.r. δ 142.9$_6$, C1; 127.5$_7$, C2; 41.5$_5$, C3; 29.1$_9$, C3Me, C4; 15.2$_7$, OCH$_2$Me; 67.9$_5$, OCH$_2$Me; 139.9$_2$, C2$\underline{C}_1$; 130.2$_8$, C2$\underline{C}_2$; 133.0$_4$, C2$\underline{C}_3$; 126.2$_1$, C2$\underline{C}_4$; 128.1$_6$, C2$\underline{C}_5$; 128.5$_1$, C2$\underline{C}_6$; 148.0$_4$, C3ipso C; 126.6$_5$, C3ortho C; 128.0$_6$, C3meta C; 125.9$_2$, C3para C.

Elution with light petroleum-ether(50:1) gave 2-(3'-chlorophenyl)-3-methyl-3-phenylbutanal(140e)(0.06g) ^{1}H n.m.r. δ 1.38, C3Me; 1.41, C4H_3; 3.68, J 3Hz, H2; 7.08, Wh/2 3Hz, ArH's; 9.68, J 3Hz, H1 and 1-(3'-chlorophenyl)-3-methyl-3-phenylbutan-2-one(139e)(0.008g) ^{1}H n.m.r. δ 1.53, C3Me, C4H_3; 3.45, C1H_2; 7.10, Wh/2 2Hz, ArH's.

Reaction of trans-1-(3',4'-dichlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89f) with BF_3-etherate in benzene

BF_3-etherate(0.25ml) was added to a solution of

trans-1-(3',4'-dichlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89f)(0.10g) in benzene(10ml) and the resulting mixture was stirred for 2 min. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(50:1) gave 2-(3',4'-dichlorophenyl)-3-methyl-3-phenylbutanal(140f)(0.064g) $\nu_{max}(CCl_4)$ 1715, 2730cm^{-1}. ^{1}H n.m.r. δ 1.41, C3Me, C4H$_3$; 3.69, J 3Hz, H2; 7.27, Wh/2 4Hz, ArH's; 9.77, J 3Hz, H1. ^{13}C n.m.r. δ 200.7$_8$, C1; 67.6$_9$, C2; 41.5$_2$, C3; 25.8$_3$, C3Me; 27.5$_5$, C4; 134.8$_2$, C2C$_1$; 132.3$_6$, C2C$_2$; n.o., C2C$_3$; n.o., C2C$_4$; 129.8$_4$, C2C$_5$; 129.8$_4$, C2C$_6$; 145.2$_8$, C3ipso C; 126.5$_3$, C3ortho C; 128.4$_2$, C3meta C; 126.8$_6$, C3para C.

Elution with light petroleum-ether(20:1) afforded 1R*,2R*-1-(3',4'-dichlorophenyl)-1-ethanoxy-3-methyl-3-phenylbutan-2-ol(189f)(0.008g) $\nu_{max}(CCl_4)$ 1060, 1090, 1120, 3550cm^{-1}. ^{1}H n.m.r. δ 1.03, J 7Hz, OCH$_2$Me; 1.27, C3Me; 1.35, C4H$_3$, OH; 3.06, Wh/2 23Hz, OCH$_2$Me; 3.50, J 3Hz, H2; 3.71, J 3Hz, H1; 7.10, Wh/2 8Hz, ArH's. ^{13}C n.m.r. δ 78.3$_6$, C1; 82.2$_2$, C2; 42.7$_2$, C3; 21.7$_3$, C3Me; 27.5$_5$, C4; 15.1$_3$, OCH$_2$Me; 64.4$_0$, OCH$_2$Me; n.o., C1C$_1$; 128.4$_6$, C1C$_2$; n.o., C1C$_3$; n.o., C1C$_4$; 129.3$_4$, C1C$_5$; 126.2$_1$, C1C$_6$; n.o., C3ipso C; 126.5$_1$, C3ortho C; 128.2$_6$, C3meta C; 125.9$_2$, C3para C.

Reaction of 2-(3',4'-dichlorophenyl)-3-methyl-3-phenylbutanal(140f) with lithium aluminium hydride

BF_3-etherate(0.5ml) was added to a solution of trans-1-(3',4'-dichlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89f)(0.16g) in benzene(15ml) and the resulting mixture was stirred for 5 min. The residue, isolated as above, was taken up in dry ether and added to a stirred suspension of lithium aluminium hydride in dry ether. The resulting mixture was heated under reflux for 0.5hr. The

residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(20:1) gave 1R*,2R*-1-(3',4'-dichlorophenyl)-1-ethanoxy-3-methyl-3-phenylbutan-2-ol (189f)(0.014g) ^{1}H n.m.r. δ 1.03, J 7Hz, $OCH_2\underline{Me}$; 1.27, C3Me; 1.35, $C4H_3$, OH; 3.06, Wh/2 23 Hz, $O\underline{CH_2}Me$; 3.50, J 3Hz, H2; 3.71, J 3Hz, H1; 7.10, Wh/2 8Hz, ArH's. Elution with ether afforded 2-(3',4'-dichlorophenyl)-3-methyl-3-phenylbutan-1-ol (153f)(0.088g) $\nu_{max}(CCl_4)$ 3620cm^{-1}. ^{1}H n.m.r. δ 1.23, C3Me, OH; 1.29, $C4H_3$; 3.00, J 5.5Hz, J 9Hz, H2; 3.72, Wh/2 7Hz, ClH_2; 7.20, Wh/2 2Hz, ArH's. ^{13}C n.m.r. δ 62.4_0, C1; 58.7_7, C2; 40.1_1, C3; 24.4_9, C3Me; 28.4_1, C4; 140.0_6, $C2\underline{C}_1$; 131.7_6, $C2\underline{C}_2$; n.o., $C2\underline{C}_3$; n.o., $C2\underline{C}_4$; 129.6_7, $C2\underline{C}_5$; 129.2_9, $C2\underline{C}_6$; 147.1_9, C3ipso C; 126.2_3, C3ortho C; 128.1_5, C3meta C; 126.2_3, C3para C.

cis-1,2-Epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(216b)

A solution of trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)(0.5g) in anhydrous deoxygenated benzene(50ml), in a quartz vessel under a nitrogen atmosphere, was irradiated(2537Å) for 2hr. After the removal of solvent, analysis by ^{1}H n.m.r. showed the presence of cis-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(109b) (50%) ^{1}H n.m.r. δ 1.38, C3Me, $C4H_3$; 3.71, ArOMe; 5.83, J 13Hz, H2; 6.41, J 13Hz, H1; 6.90, ArH's and trans-1-(4'-methoxyphenyl)-3-methyl-3-phenylbut-1-ene(88b)(50%) ^{1}H n.m.r. δ 1.50, C3Me, $C4H_3$; 3.70, ArOMe; 6.30, H1, H2; 7.05, ArH's.

The reaction product was taken up in ether and m-chloroperbenzoic acid(0.4g) was added. The resulting mixture was stirred at 4°C for 4 days. Sodium bicarbonate solution was added and the mixture was stirred for 15 min. The ethereal layer was separated, washed with sodium bicarbonate solution and water and dried over anhydrous

magnesium sulphate. The residue, isolated on the removal of the solvent, was absorbed onto alumina(80g). Elution with light petroleum-ether(50:1) gave trans-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(89b)(0.18g) ^{1}H n.m.r. δ 1.40, C3Me; 1.50, $C4H_3$; 3.04, J 2Hz, H2; 3.72, J 2Hz, H1; 3.77, ArOMe; 7.10, Wh/2 31Hz, ArH's.

Further elution afforded cis-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(216b)(0.15g) (Found: M^+, 268.1423; C, 80.6; H, 7.5. $C_{18}H_{20}O_2$ requires M^+, 268.1462; C, 80.6; H, 7.5%). $\nu_{max}(CCl_4)$ 840cm^{-1}. ^{1}H n.m.r. δ 1.05, C3Me; 1.10, $C4H_3$; 3.10, J 4Hz, H2; 3.75, ArOMe; 4.02, J 4Hz, H1; 7.05, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 57.9_6, C1; 66.6_4, C2; 39.1_9, C3; 24.9_7, C3Me; 27.1_9, C4; 55.2_0, ArOMe; 128.4_5, C1ipso C; 127.6_7, C1ortho C; 113.4_1, C1meta C; 158.7_2, C1para C; 147.6_2, C3ipso C; 126.0_6, C3ortho C; 128.1_0, C3meta C; 126.0_6, C3para C.

Reaction of cis-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane(216b) with BF_3-etherate in benzene

BF_3-etherate(0.25ml) was added to a solution of cis-1,2-epoxy-1-(4'-methoxyphenyl)-3-methyl-3-phenylbutane (216b)(0.08g) in benzene and the resulting mixture was stirred for 2 min. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(50:1) afforded 1-(4'-methoxyphenyl)-3-methyl-3-phenylbutan-2-one(139b)(0.008g) ^{1}H n.m.r. δ 1.50, C3Me, $C4H_3$; 3.42, $C1H_2$; 3.72, ArOMe; 6.82, C1ArH's; 7.20, C3ArH's and 2-(4'-methoxyphenyl)-3-methyl-3-phenylbutanal(140b)(0.058g) ^{1}H n.m.r. δ 1.35, C3Me; 1.42, $C4H_3$; 3.65, J 3.5Hz, H2; 3.75, ArOMe; 6.80, C2ArH's; 7.25, C3ArH's; 9.70, J 3.5Hz, H1 which were identical to authentic samples.

cis-1-(4'-Chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(216d)

A solution of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(0.46g) in t-butyl alcohol(50ml) was irradiated(2537Å) as above for 3hr. After the removal of solvent, analysis by ^{1}H n.m.r. showed the presence of trans-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88d)(47%) ^{1}H n.m.r. δ 1.47, C3Me, C4H$_3$; 6.33, H1, H2; 7.22, Wh/2 2Hz, ArH's, cis-1-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene (109d)(33%) ^{1}H n.m.r. δ 1.36, C3Me, C4H$_3$; 5.92, J 13Hz, H2; 6.41, J 13Hz, H1; 7.03, Wh/2 4Hz, ArH's and trans-1-(4'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112d)(20%) ^{1}H n.m.r. δ 0.96, C3Me; 2.31, H1, H2; 7.23, Wh/2 4Hz, ArH's.

The reaction product was taken up in ether and m-chloroperbenzoic acid(0.2g) was added. The resulting mixture was stirred for 4 days at 4°C. The residue, isolated as above, was absorbed onto alumina(80g). Elution with light petroleum gave trans-1-(4'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112d)(0.14g). Elution with light petroleum-ether(50:1) afforded trans-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(89d)(0.15g) ^{1}H n.m.r. δ 1.25, C3Me; 1.35, C4H$_3$; 2.81, J 2Hz, H2; 3.55, J 2Hz, H1; 7.15, Wh/2 7Hz, ArH's and cis-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(216d)(0.10g) ν_{max}(CCl_4) 850cm^{-1}. ^{1}H n.m.r. δ 1.10, C3Me; 1.14, C4H$_3$; 3.26, J 4.5Hz, H2; 4.01, J 4.5Hz, H1; 7.15, ClArH's; 7.22, C3ArH's. ^{13}C n.m.r. δ 66.6$_4$, C1; 57.5$_7$, C2; 39.0$_1$, C3; 25.4$_2$, C3Me; 27.0$_4$, C4; 134.0$_7$, C1ipso C; 127.8$_7$, C1ortho C; 127.9$_8$, C1meta C; 132.6$_0$, C1para C; 146.7$_1$, C3ipso C; 126.1$_4$, C3ortho C; 127.9$_8$, C3meta C; 126.0$_7$, C3para C.

Reaction of cis-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(216d) with BF_3-etherate in benzene

BF_3-etherate(0.25ml) was added to a solution of cis-1-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane (216d)(0.07g) in benzene(10ml) and the resulting mixture was stirred for 2 min. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(50:1) afforded 1-(4'-chlorophenyl)-3-methyl-3-phenyl-butan-2-one(139d)(c. 0.002g) ^{1}H n.m.r. δ 1.52, C3Me, $C4H_3$; 3.44, ClH_2; 7.02, Wh/2 6Hz, ArH's and 2-(4'-chlorophenyl)-3-methyl-3-phenylbutanal(140d)(0.05g) ^{1}H n.m.r. δ 1.42, C3Me, $C4H_3$; 3.72, J 2Hz, H2; 7.07, Wh/2 3Hz, ArH's; 9.73, J 2Hz, H1 which were identical to authentic samples.

cis-1-(3'-Chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(216e)

A solution of trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(88e)(0.64g) in t-butyl alcohol(50ml) was irradiated(2537Å), as above, for 3hr. The solvent was removed and analysis by ^{1}H n.m.r. showed the presence of trans-1-(3'-chlorophenyl)-3-methyl-3-phenylbutane(88e)(33%) ^{1}H n.m.r. δ 1.45, C3Me, $C4H_3$; 6.30, H1, H2; 7.10, Wh/2 12Hz, ArH's, cis-1-(3'-chlorophenyl)-3-methyl-3-phenylbutane(109e)(33%) ^{1}H n.m.r. δ 1.36, C3Me, $C4H_3$; 5.91, J 13Hz, H2; 6.39, J 13Hz, H1; 7.16, Wh/2 6Hz, ArH's and trans-1-(3'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112e)(33%) ^{1}H n.m.r. δ 0.95, C3Me; 2.35, H1, H2; 7.19, Wh/2 6Hz, ArH's.

The reaction product was taken up in ether and m-chloroperbenzoic acid(0.2g) was added. The resulting mixture was stirred for 4 days at 4°C. The residue, isolated as above, was absorbed onto alumina(80g). Elution with light petroleum gave trans-1-(3'-chlorophenyl)-3,3-dimethyl-2-phenylcyclopropane(112e)(0.20g). Elution with light petroleum-

ether(50:1) afforded trans-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbut-1-ene(89e)(0.36g) ^{1}H n.m.r. δ 1.28, C3Me; 1.35, C4H$_3$; 2.90, J 2Hz, H2; 3.64, J 2Hz, H1; 7.15, Wh/2 14Hz, ArH's and cis-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(216e)(0.12g) ν_{max}(CCl_4) 820cm^{-1}. ^{1}H n.m.r. δ 1.15, C3Me, C4H$_3$; 3.25, J 4Hz, H2; 3.98, J 4Hz, H1; 7.10, ClArH's; 7.20, C3ArH's. ^{13}C n.m.r. δ 66.6$_3$, C1; 57.4$_4$, C2; 38.8$_9$, C3; 25.6$_7$, C3Me; 26.8$_8$, C4; 137.5$_2$, Cl$\underline{C}_1$; 126.7$_8$, Cl$\underline{C}_2$; 133.8$_2$, Cl$\underline{C}_3$; 127.1$_3$, Cl$\underline{C}_4$; 129.0$_1$, Cl$\underline{C}_5$; 124.6$_2$, Cl$\underline{C}_6$; 146.3$_1$, C3ipso C; 126.1$_5$, C3ortho C; 127.9$_0$, C3meta C; 126.2$_5$, C3para C.

Reaction of cis-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(216e) with BF_3-etherate in benzene

BF_3-etherate(0.25ml) was added to a solution of cis-1-(3'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane (216e)(0.09g) in benzene(10ml) and the resulting mixture was stirred for 2 min. The residue, isolated as above, was 2-(3'-chlorophenyl)-3-methyl-3-phenylbutanal(140e)(0.06g) ^{1}H n.m.r. δ 1.38, C3Me; 1.41, C4H$_3$; 3.68, J 3Hz, H2; 7.08, Wh/2 3Hz, ArH's; 9.68, J 3Hz, H1 which was identical to an authentic sample.

Reaction of 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144) with boron trifluoride etherate in benzene

(i) BF_3-etherate(0.25ml) was added to a solution of 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144)(0.21g) in benzene(15ml) and the resulting mixture was stirred for 5 min. Saturated potassium carbonate solution was added and the resulting mixture was stirred for 0.5hr. The solution was dried over anhydrous potassium carbonate and filtered. The solvent was removed and the residue absorbed onto alumina (80g). Elution with light petroleum afforded 2,4-diphenyl-4-methylpent-1-ene(227)(0.016g) (Found: M^+, 236.1529; C, 91.5; H, 8.6. $C_{18}H_{20}$ requires M^+, 236.1564; C, 91.5; H, 8.5%). $\nu_{max}(CCl_4)$ 895cm^{-1}. ^{1}H n.m.r. δ 1.20, C4Me, $C5H_3$; 2.80, $C3H_2$; 4.72, Wh/2 4Hz, H1; 5.08, J 2Hz, H1'; 7.12, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 116.8_7, C1; 149.4_0, C2; 49.6_4, C3; 38.6_7, C4; 28.7_6, C4Me, C5; 143.7_4, C2ipso C; 125.9_2, C2ortho C; 127.8_2, C2meta C; 126.8_4, C2para C; 146.7_4, C4ipso C; 126.5_4, C4ortho C; 128.0_1, C4meta C; 125.9_2, C4para C.

Elution with light petroleum-ether(20:1) gave benzophenone(46)(0.046g) $\nu_{max}(CCl_4)$ 1665cm^{-1}. ^{1}H n.m.r. δ 7.65, Wh/2 14Hz, ArH's. Elution with ether afforded 4-phenylpentan-2-ol(226)(0.042g) (Found: M^+, 164.1185; C, 80.1; H, 9.8%). $\nu_{max}(CCl_4)$ 3650cm^{-1}. ^{1}H n.m.r. δ 1.15, J 6Hz, $C5H_3$; 1.25, J 6Hz, $C1H_3$; 1.40, OH; 1.80, Wh/2 20Hz, $C3H_2$; 2.82, Wh/2 22Hz, H4; 3.67, Wh/2 15Hz, H2; 7.03, ArH's. ^{13}C n.m.r. δ 23.6_5, C1; 66.2_8, C2; 47.8_2, C3; 36.8_8, C4; 22.3_3, C5; 147.2_8, C4ipso C; 126.8_7, C4ortho C; 128.5_3, C4meta C; 126.0_9, C4para C.

(ii) BF_3-etherate(0.25ml) was added to a solution of 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144)(0.29g) in benzene(25ml) and the resulting mixture was stirred for

2 min. The product, isolated as above, was absorbed onto alumina(80g). Elution with light petroleum-ether(50:1) gave 2-phenylpropyl-2-ethyl ether(218)(0.016g) ^{1}H n.m.r. δ 1.12, J 7Hz, $OCH_2\underline{Me}$; 1.52, $C1H_3$, $C3H_3$; 3,20, J 7Hz, $O\underline{CH_2}Me$; 7.25, Wh/2 10Hz, ArH's. Further elution gave 2-phenylpropyl-2-(2,2-diphenylethylene)ether(217)(0.110g) (Found: M^+, 314.1645; C, 87.6; H, 7.1. $C_{23}H_{20}O$ requires M^+, 314.1669; C, 87.9; H, 7.1%). $\nu_{max}(CCl_4)$ 790, 1065, 1090, 1110cm^{-1}. ^{1}H n.m.r. δ 1.65, $C1H_3$, $C3H_3$; 6.35, C4H; 7.25, Wh/2 16Hz, ArH's. ^{13}C n.m.r. δ 29.0_0, C1, C3; 80.7_1, C2; 140.7_2, C4; 120.6_9, C5; 145.4_5, C2ipso C; 125.7_3, C2ortho C; 128.3_7, C2meta C; 127.2_5, C2para C; 138.1_2, C5ipso C's; 129.9_2, 128.5_1, C5ortho C's; 128.0_7, 127.7_8, C5meta C's; 126.1_7, C5para C's.

Elution with light petroleum-ether(20:1) afforded 3-methyl-1,1,3-triphenylbutan-2-one(146)(0.020g) (Found: M^+, 167.0844 and 147.0696. $C_{23}H_{22}O$ requires M^+, 314.1669; $M^+-C_{10}H_{11}O$ requires 167.0860; $M^+-C_{13}H_{11}$ requires 147.0809). $\nu_{max}(CCl_4)$ 1715cm^{-1}. ^{1}H n.m.r. δ 1.44, C3Me, $C4H_3$; 5.06, H1; 7.07, Wh/2 11Hz, ArH's. ^{13}C n.m.r. δ 58.7_2, C1; 209.8_1, C2; 53.7_0, C3; 24.9_8, C3Me, C4; 139.8_1, C1ipso C; 128.3_9, C1ortho C; 128.3_0, C1meta C; 126.9_6, C1para C; 142.5_6, C3ipso C; 126.6_9, C3ortho C; 128.6_4, C3meta C; 127.1_3, C3para C. Further elution gave benzophenone(46)(0.070g) $\nu_{max}(CCl_4)$ 1665cm^{-1}. ^{1}H n.m.r. δ 7.65, Wh/2 14Hz, ArH's.

NOTE: The ^{1}H n.m.r. and i.r. spectra of the crude reaction products of these reactions indicate the presence of aldehyde products. In reaction (i), aldehyde, $\nu_{max}(CCl_4)$ 1725, 2720, 2820cm^{-1}; ^{1}H n.m.r. δ 4.69, J 2.5Hz,; 9.80, J 2.5Hz was detected(c. 15%). In reaction (ii), aldehyde, $\nu_{max}(CCl_4)$ 1715, 2710, 2810cm^{-1}; ^{1}H n.m.r. δ 9.87(s), was

detected (c. 5%).

Reaction of 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144) with BF_3-etherate in ether

BF_3-etherate(0.25ml) was added to a solution of 1,2-epoxy-3-methyl-1,1,3-triphenylbutane(144)(0.082g) in ether(10ml) and the resulting solution was stirred for 0.5hr. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum-ether(100:1) afforded 2-phenylpropyl-2-(2,2-diphenylethylene)ether(217) (0.039g) ^{1}H n.m.r. δ 1.65, ClH_3, $C3H_3$; 6.35, C4H; 7.25, Wh/2 16Hz, ArH's. Further elution with light petroleum-ether (20:1) gave benzophenone(46)(0.016g) $\nu_{max}(CCl_4)$ 1665cm^{-1}; ^{1}H n.m.r. δ 7.65, Wh/2 14Hz, ArH's. The aldehyde detected by ^{1}H n.m.r. δ 9.80, J 2.5Hz; 4.69, J 2.5Hz, (c. 5%) was not isolated by column chromotography.

Reaction of 2-phenylpropyl-2-(2,2-diphenylethylene)ether(217) with BF_3-etherate in benzene

BF_3-etherate(0.25ml) was added to a solution of 2-phenylpropyl-2-(2,2-diphenylethylene)ether(217)(0.03g) in benzene(10ml) and the resulting mixture was stirred for 5 min. The ^{1}H n.m.r. spectrum of the crude reaction product, isolated as above, showed the presence of the previously observed but undetermined aldehyde, δ_H 9.80, J 2.5Hz; 4.69, J 2.5Hz and 2,4-diphenyl-4-methylpent-1-ene(227) δ_H 1.20, C4Me, $C5H_3$; 2.80, $C3H_2$; 4.72, Wh/2 4Hz, H1; 5.08, J 2Hz, H1' in a ratio c. 1:2, determined by integration of the peaks at δ 9.79 and 5.08. The i.r. spectrum of the reaction product showed the presence of 4-phenylpentan-2-ol(226) $\nu_{max}(CCl_4)$ 3650cm^{-1} and benzophenone(46) $\nu_{max}(CCl_4)$ 1665cm^{-1}.

1,1-Di-(4'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(233)

A solution of p-bromochlorobenzene(12g) in dry tetrahydrofuran was added slowly to a stirred suspension of magnesium(1.5g) in dry tetrahydrofuran. The resulting mixture was heated under reflux for 0.5hr and cooled to room temperature. A solution of methyl-3-methyl-3-phenylbutanoate(232)[58](5g) in dry tetrahydrofuran was added slowly and resulting mixture heated gently for 4hr and stirred at room temperature overnight. The mixture was poured onto saturated ammonium chloride solution and the organic layer was isolated. The aqueous layer was extracted with ether and the combined organic fractions were washed with water and saturated sodium chloride solution and dried over anhydrous magnesium sulphate. The solvent was removed and the residue absorbed onto alumina(160g). Elution with light petroleum-ether(10:1) afforded 1,1-di-(4'-chlorophenyl)-3-methyl-3-phenylbutan-1-ol(233)(5.3g) (Found: M^+, 366.0939. $C_{23}H_{22}Cl_2O$ requires M^+, 384.1045; M^+-H_2O requires 366.0940). ν_{max}(neat) 3580cm^{-1}. ^{1}H n.m.r. δ 1.07, C3Me, C4H$_3$; 1.77, OH; 2.75, Wh/2 3Hz, C2H$_2$; 7.10, Wh/2 3Hz, ArH's. ^{13}C n.m.r. δ 77.3$_5$, C1; 53.7$_6$, C2; 37.8$_5$, C3; 30.8$_6$, C3Me, C4; 146.5$_9$, C1ipso C; 125.8$_4$, C1ortho C; 128.0$_4$, C1meta C; 132.3$_3$, C1para C; 148.4$_4$, C3ipso C; 126.9$_1$, C3ortho C; 128.5$_7$, C3meta C; 126.1$_2$, C3para C.

1,1-Di-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(234)

p-Toluenesulphonic acid(0.5g) was added to a solution of 1,1-di-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ol(233) (3.0g) in benzene and the resulting mixture was heated under reflux for 0.5hr. The oil, isolated as previously described, was 1,1-di-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(234) (2.5g) (Found: C, 75.3; H, 5.3. $C_{23}H_{20}Cl_2$requires C,75.4;

H, 5.5%). ν_{max}(neat) 825cm^{-1}. ^{1}H n.m.r. δ 1.28, C3Me, C4H$_3$; 6.35, H2; 6.95, Wh/2 6Hz, ArH's. ^{13}C n.m.r. δ 140.5$_2$, Cl; 137.8$_4$, C2; 40.6$_3$, C3; 30.9$_1$, C3Me, C4; 141.6$_9$, 138.5$_7$, Clipso C's; 131.2$_0$, 127.7$_8$, Clortho C's; 128.1$_4$, Clmeta C's; 132.8$_5$, 132.7$_0$, Clpara C's; 149.9$_1$, C3ipso C; 125.9$_8$, C3ortho C; 127.9$_8$, C3meta C; 125.5$_4$, C3para C.

1,1-Di-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(230)

m-Chloroperbenzoic acid(1g) was added to a solution of 1,1-di-(4'-chlorophenyl)-3-methyl-3-phenylbut-1-ene(234) (2gm) in ether and the resulting mixture was stirred at 4^{o}C for 4 days. The product, isolated as previously described, was absorbed onto an alumina dry column(80g). Light petroleum-ether(50:1) was allowed to percolate through the column. Elution of the segment c. Rf 0.15 to 0.8 afforded 1,1-di-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(230) (0.69g) (Found: C, 71.8; H, 5.1. $C_{23}H_{20}Cl_2O$ requires C, 72.2, H, 5.3%). ^{1}H n.m.r. δ 1.05, C3Me; 1.18, C4H$_3$; 3.42, H2; 7.12, Wh/2 8Hz, ArH's. ^{13}C n.m.r. δ 65.2$_3$, Cl; 74.2$_0$, C2; 38.9$_7$, C3; 24.1$_7$, C3Me; 28.2$_0$, C4; 140.1$_7$, 135.2$_0$, Clipso C's; 128.4$_6$, 128.0$_2$, Clortho C's; 129.2$_4$, 127.7$_8$, Clmeta C's; 133.5$_7$, 133.3$_4$, Clpara C's; 146.5$_7$, C3ipso C; 125.8$_7$, C3ortho C; 128.1$_1$, C3meta C; 126.2$_2$, C3para C.

Reaction of 1,1-di-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(230) with BF_3-etherate in benzene

(i) BF_3-etherate(0.25ml) was added to a solution of 1,1-di-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane(230)(0.165g) in benzene(15ml) and the resulting mixture was stirred for 5 min. The product, isolated as previously described, was absorbed onto alumina(13g). Elution with light petroleum afforded 2,4-diphenyl-4-methyl-

pent-1-ene(227)(0.035g) ^{1}H n.m.r. δ 1.20, C4Me, $C5H_3$; 2.80, $C3H_2$; 4.72, Wh/2 4Hz, H1; 5.08, J 2Hz, H1'; 7.12, Wh/2 3Hz, ArH's. Further elution with light petroleum-ether(50:1) gave bis-(4'-chlorophenyl)ketone(235)(0.057g) $\nu_{max}(CCl_4)$ 1668cm^{-1}. ^{1}H n.m.r. δ 7.50, Wh/2 11Hz, ArH's. ^{13}C n.m.r. δ 194.0_3, Cl; 135.5_1, Cl*ipso* C's; 131.2_5, Cl*ortho* C's; 128.7_3, Cl*meta* C's; 139.1_0, Cl*para* C's.

(ii) BF_3-etherate(0.25ml) was added to a solution of 1,1-di-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane (230)(0.144g) in benzene and the resulting mixture was stirred for 2 min. The residue, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum afforded 2,4-diphenyl-4-methylpent-1-ene(227)(0.031g) ^{1}H n.m.r. δ 1.20, C4Me, $C5H_3$; 2.80, $C3H_2$; 4.72, Wh/2 4Hz, H1; 5.08, J 2Hz, H1'; 7.12, Wh/2 3Hz, ArH's. Further elution with light petroleum-ether(50:1) gave bis-(4'-chlorophenyl)-ketone(235)(0.043g) $\nu_{max}(CCl_4)$ 1668cm^{-1}. ^{1}H n.m.r. δ 7.50, Wh/2 11Hz, ArH's.

(iii) BF_3-etherate(0.25ml) was added to a solution of 1,1-di-(4'-chlorophenyl)-1,2-epoxy-3-methyl-3-phenylbutane (230)(0.17g) in benzene(15ml) and the resulting mixture was stirred for 0.5 min. The product, isolated as above, was absorbed onto alumina(13g). Elution with light petroleum afforded 2,4-diphenyl-4-methylpent-1-ene(237)(0.004g) ^{1}H n.m.r. δ 1.20, C4Me, $C5H_3$; 2.80, $C3H_2$; 4.72, Wh/2 4Hz, H1; 5.08, J 2Hz, H1'; 7.12, Wh/2 3Hz, ArH's. Further elution gave 2-phenylpropyl-2-(2,2-di-(4'-chlorophenyl)ethylene)ether (238)(0.043g) (Found: M^+, 263.0009 and 119.0853. $C_{23}H_{20}Cl_2O$ requires M^+, 382.0889; $M^+-C_9H_{11}$ requires 263.0031; $M^+-C_{14}H_9Cl_2O$ requires 119.0860). $\nu_{max}(CCl_4)$ 1150cm^{-1}. ^{1}H n.m.r. δ 1.65, $C1H_3$, $C3H_3$; 6.25, H4; 7.07, Wh/2 2Hz, ArH's.

^{13}C n.m.r. δ 29.0_0, C1; 81.2_5, C2; 29.0_0, C3; 141.4_0, C4; 118.5_9, C5; 145.1_0, C2ipso C; 125.7_3, C2ortho C; 128.4_1, C2meta C; 127.5_3, C2para C; 136.1_7, C5ipso C's; 131.1_4, 129.7_1, C5ortho C's; 128.5_1, 128.1_1, C5meta C's; 132.2_2, C5para C's. Elution with light petroleum-ether(50:1) afforded bis-(4'-chlorophenyl)ketone(235)(0.048g) $\nu_{max}(CCl_4)$ 1668cm^{-1}. ^{1}H n.m.r. δ7.50, Wh/2 11Hz, ArH's.

NOTE: The ^{1}H n.m.r. and i.r. spectra of the crude reaction products in each reaction indicated the presence of an aldehyde(c. 20%) $\nu_{max}(CCl_4)$ 1725, 2720, 2820cm^{-1}. ^{1}H n.m.r. δ 4.80, Wh/2 5Hz; 9.83, J 2Hz; which could not be isolated by column chromotography.

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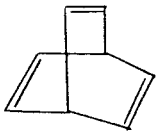

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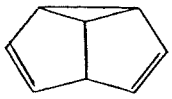

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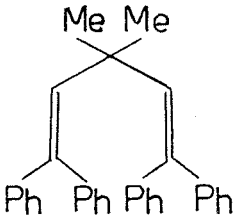

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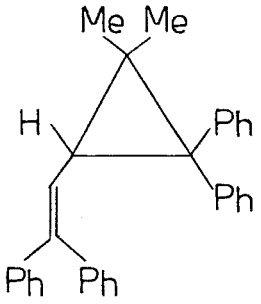

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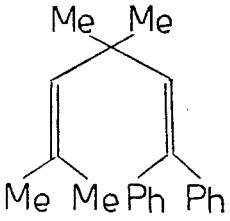

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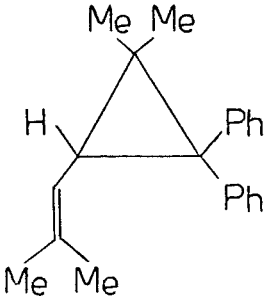

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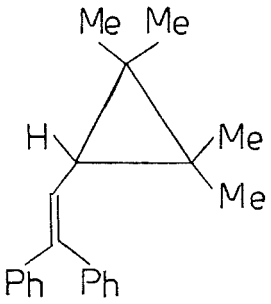

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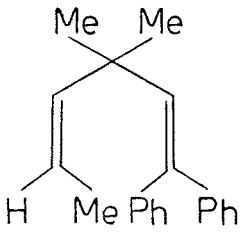

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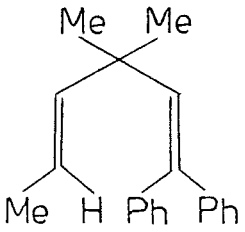

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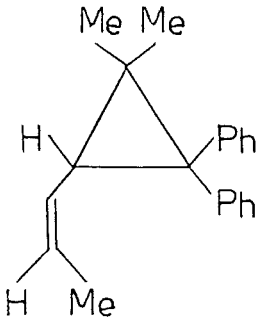

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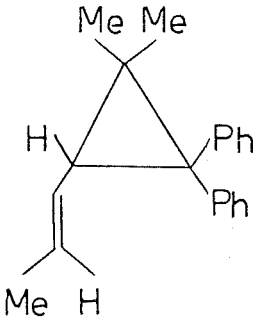

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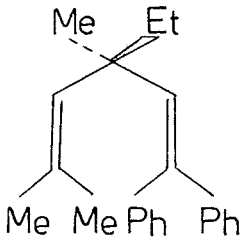

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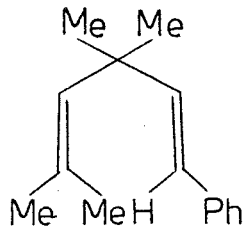

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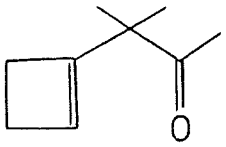

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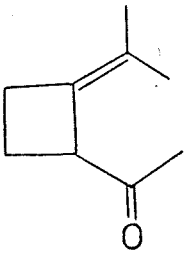

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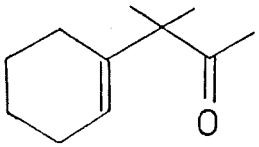

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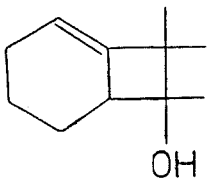

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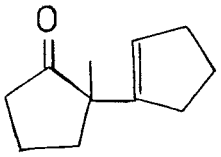

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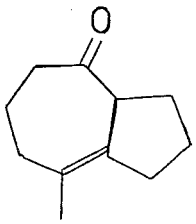

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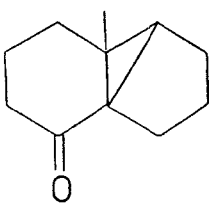

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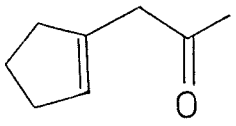

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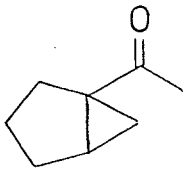

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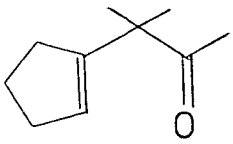

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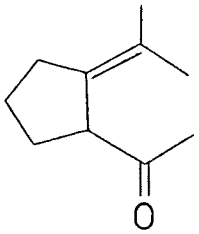

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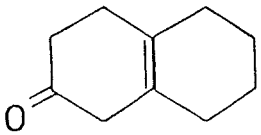

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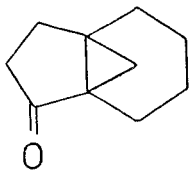

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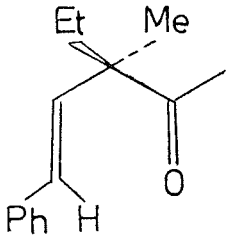

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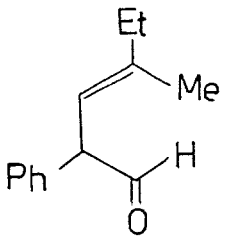

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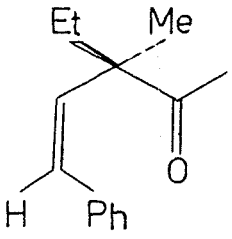

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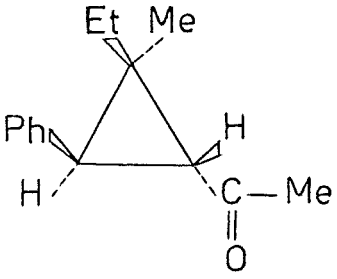

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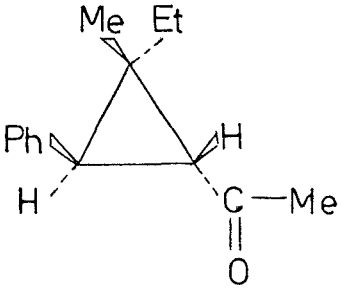

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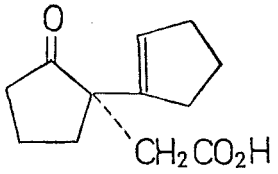

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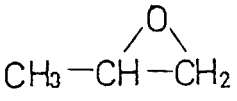

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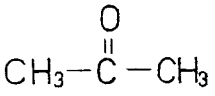

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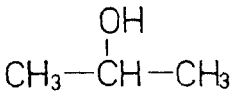

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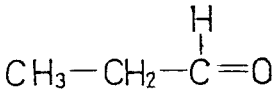

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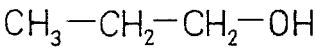

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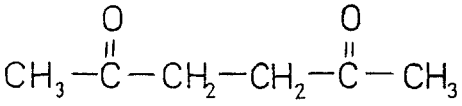

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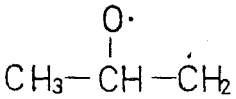

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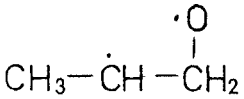

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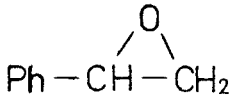

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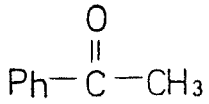

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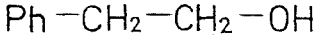

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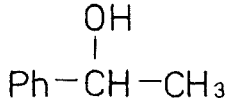

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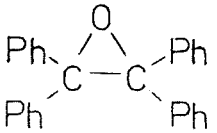

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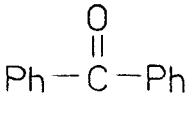

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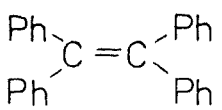

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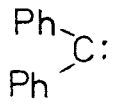

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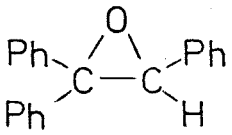

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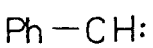

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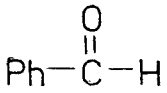

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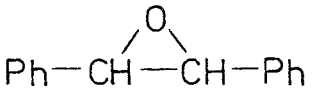

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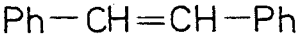

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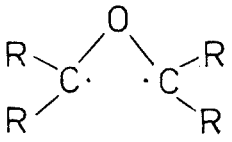

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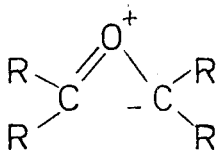

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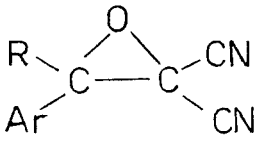

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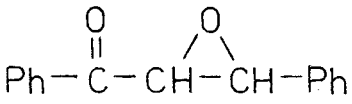

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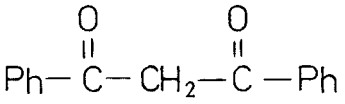

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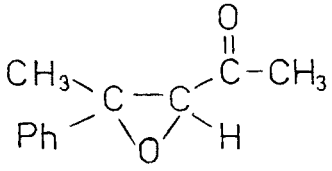

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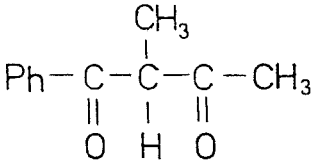

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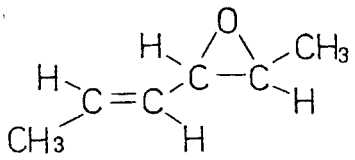

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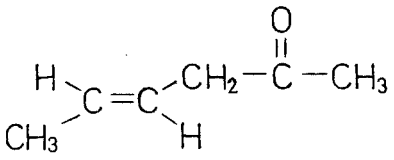

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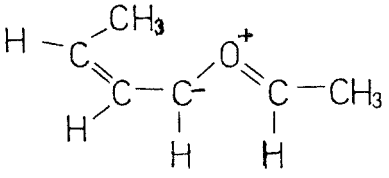

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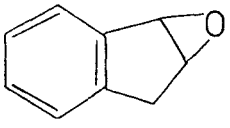

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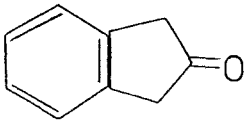

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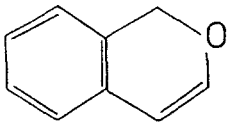

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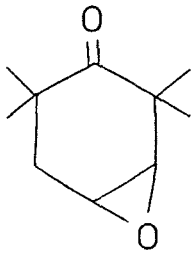

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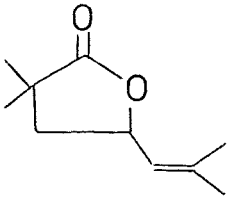

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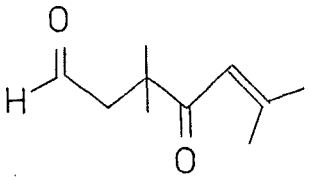

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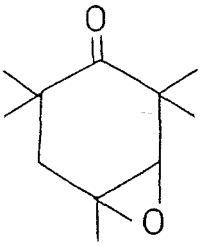

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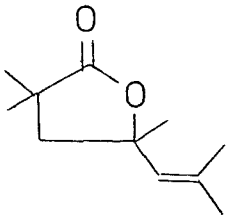

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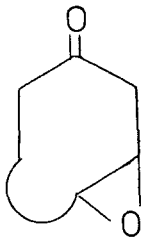

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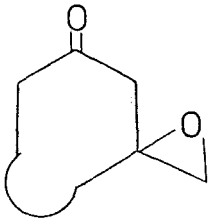

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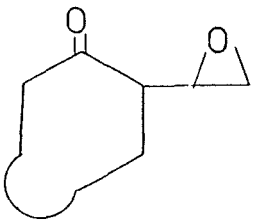

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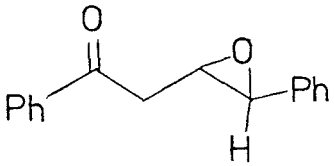

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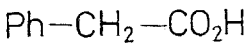

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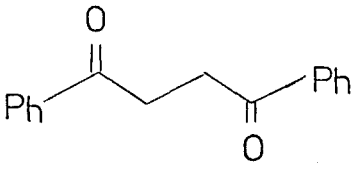

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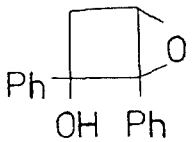

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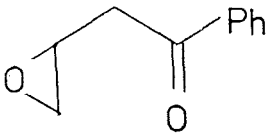

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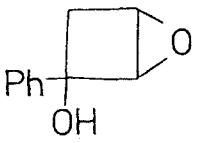

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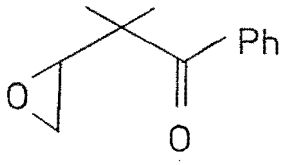

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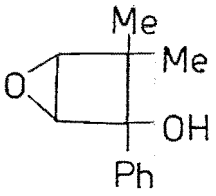

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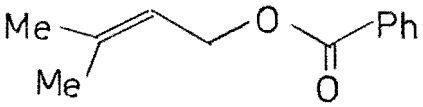

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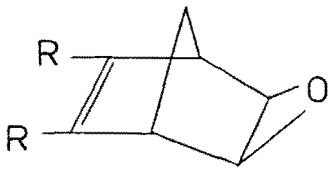

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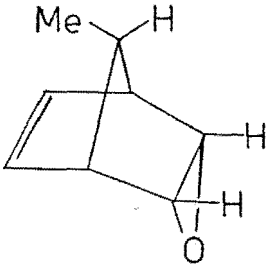

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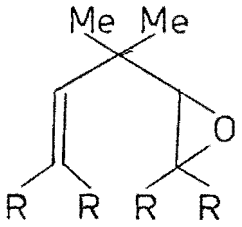

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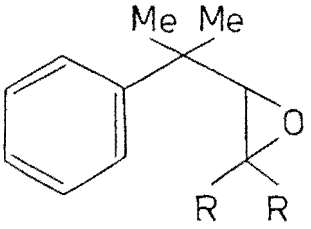

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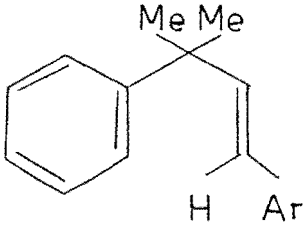
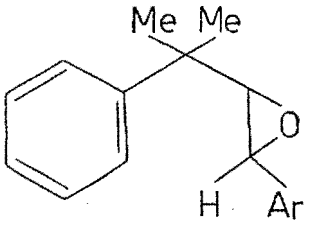


88

Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl
(f) 3',4'-Ph-Cl_2
(g) p-Ph-CN



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Ar: (a) Ph-H
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(c) p-Ph-Me
(d) p-Ph-Cl
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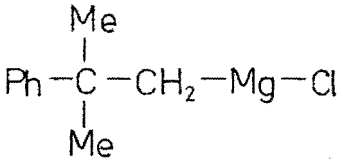

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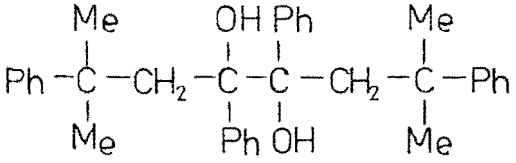

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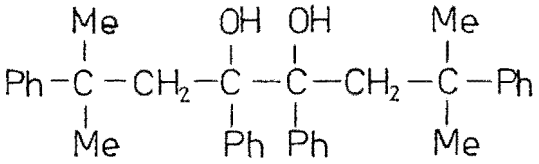
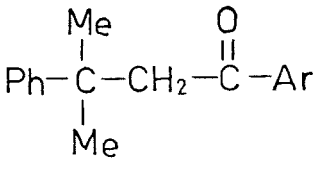
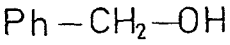


91(b) meso

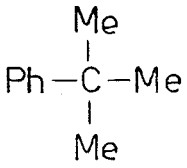


92

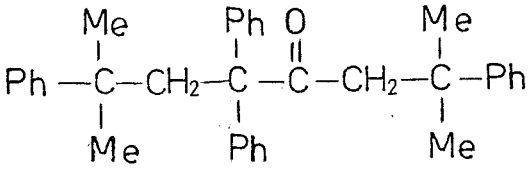
Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl



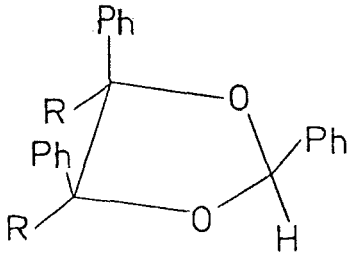
93



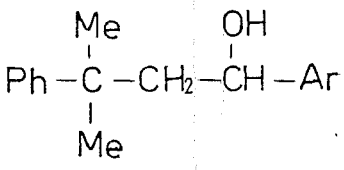
94



95

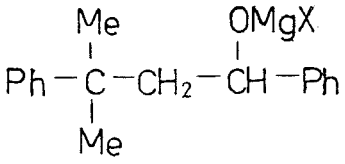


96

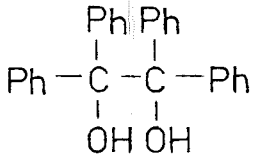


97

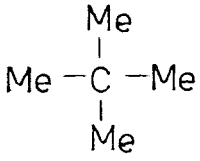
Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl
(f) 3',4'-Ph-Cl_2



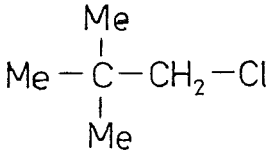
98



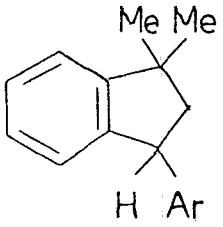
99



100

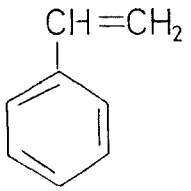


101

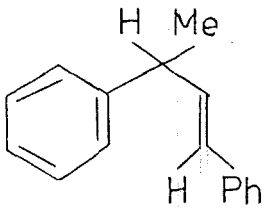


102

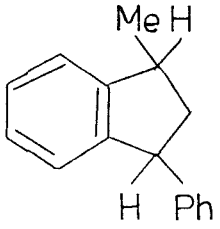
Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl
(f) 3',4'-Ph-Cl_2



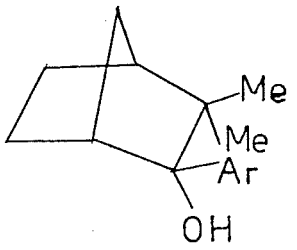
103



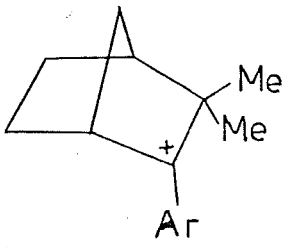
104



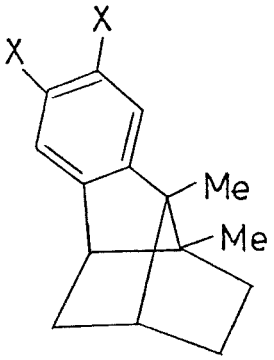
105



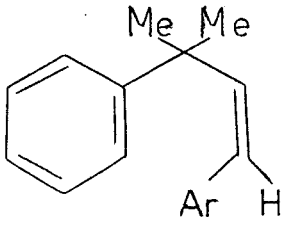
106



107

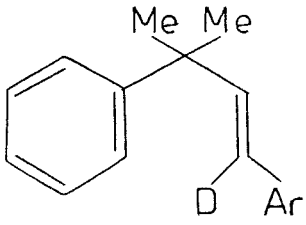


108



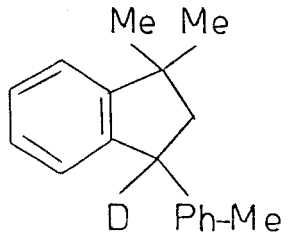
109

Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl
(f) 3',4'-Ph-Cl_2
(g) p-Ph-CN

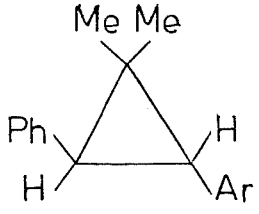


110

Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl

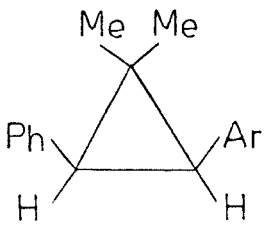


111



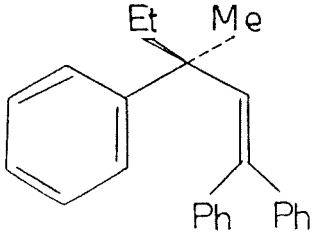
112

Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl
(f) 3',4'-Ph-Cl_2
(g) p-Ph-CN

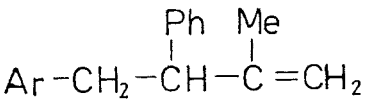


113

Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl
(f) 3',4'-Ph-Cl_2
(g) p-Ph-CN

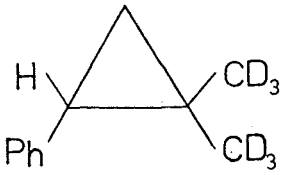


114

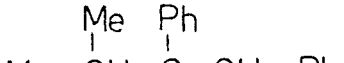


115

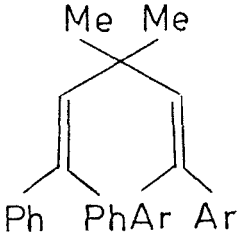
Ar: (a) Ph-H
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl
(g) p-Ph-CN



116

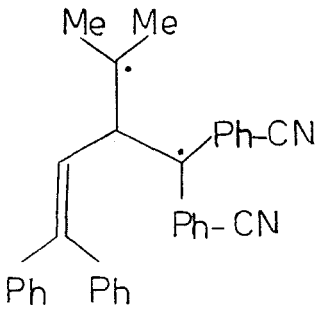


117

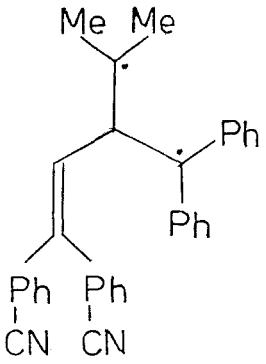


118

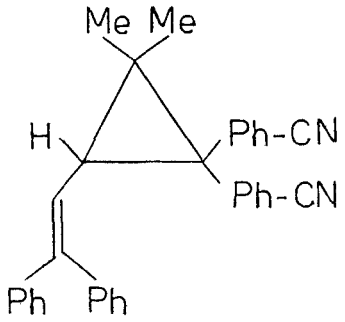
Ar: (a) p-Ph-OMe
(b) p-Ph-CN



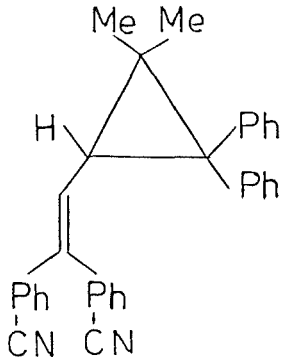
119



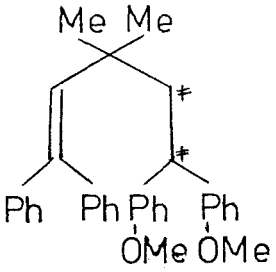
120



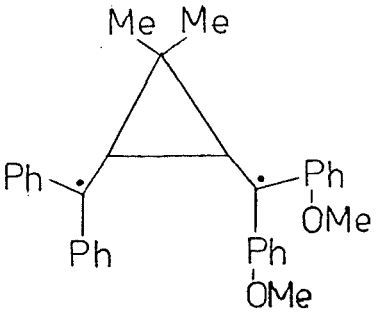
121



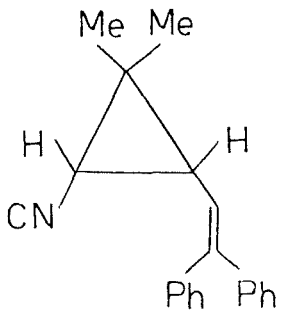
122



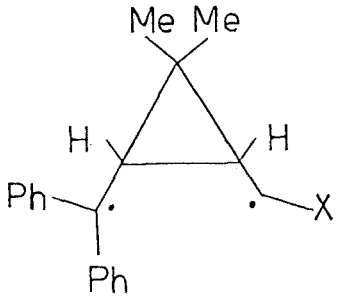
123



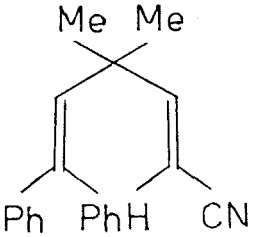
124



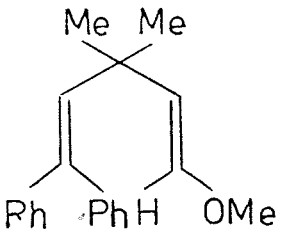
125



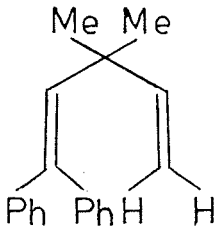
126



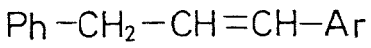
127



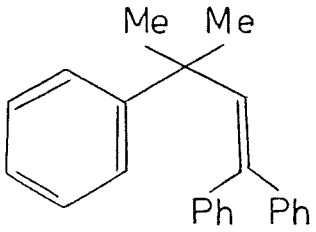
128



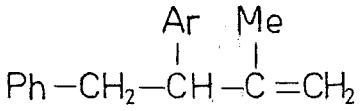
129



130

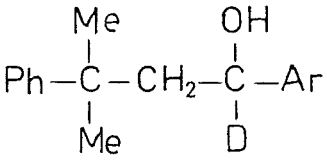


131



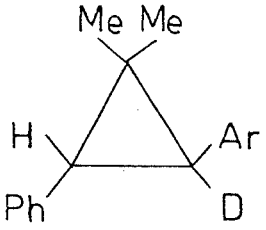
132

Ar: (c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl
(f) p-Ph-CN

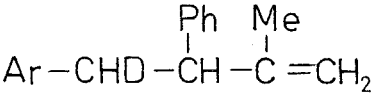


133

Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl

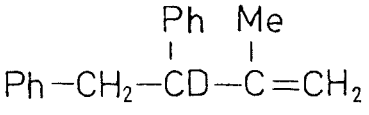


134

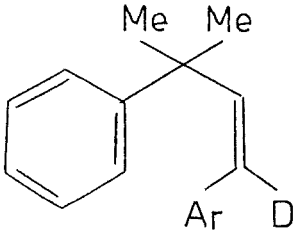


135

Ar: (a) Ph-H
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl

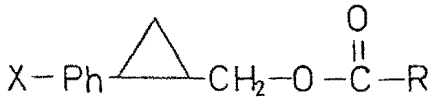


136

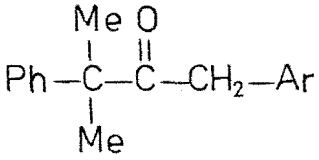


137

Ar: (a) Ph-H
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl

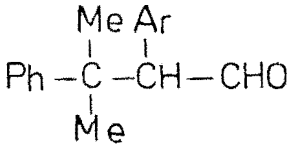


138



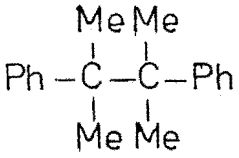
139

Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl

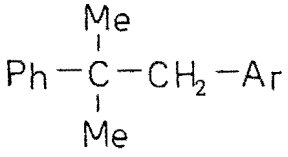


140

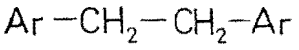
Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph- Cl
(f) 3',4'-Ph-Cl_2



141

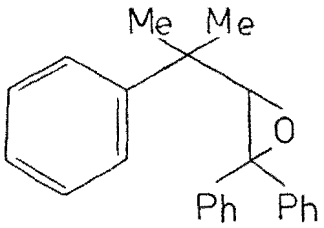


142



143

Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl



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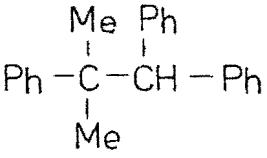

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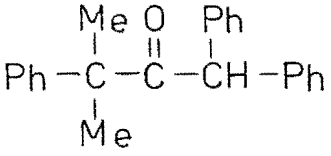

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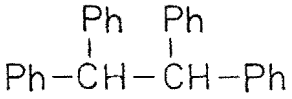

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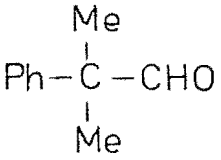

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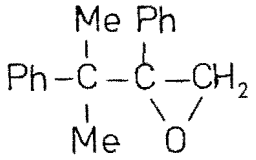

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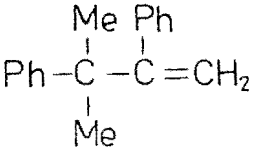

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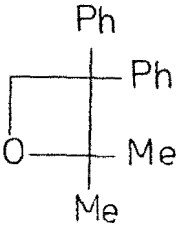

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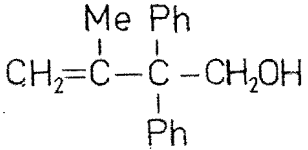

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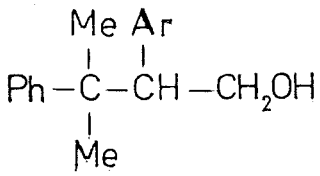
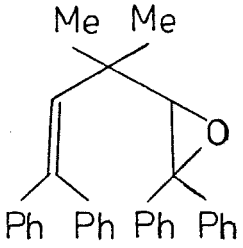


153

Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(e) m-Ph-Cl
(f) 3',4'-Ph-Cl2



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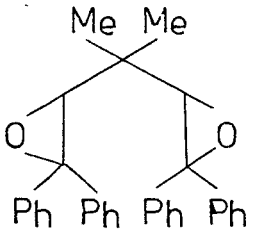

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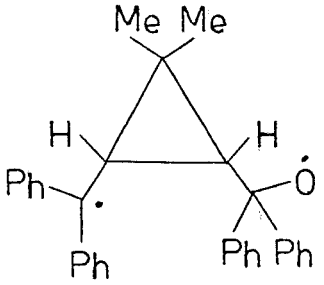

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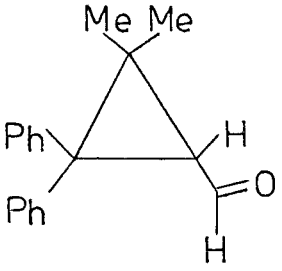

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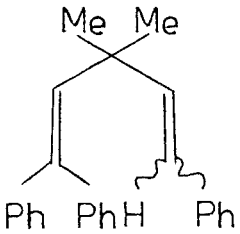

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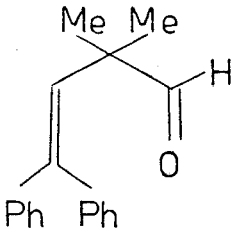

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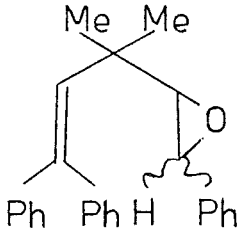

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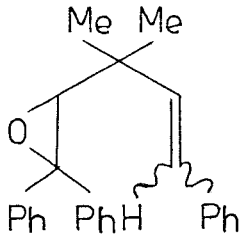

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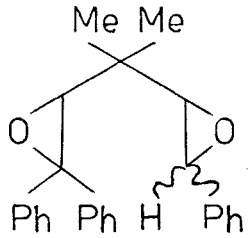

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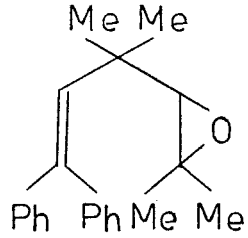

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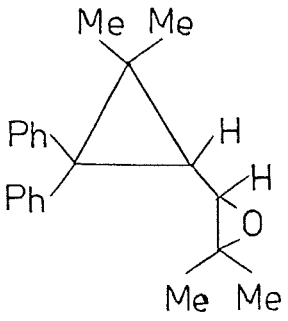

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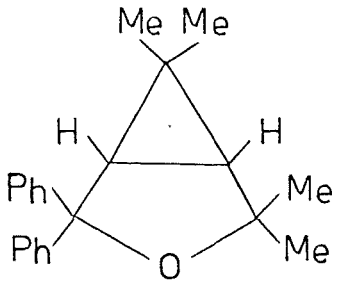

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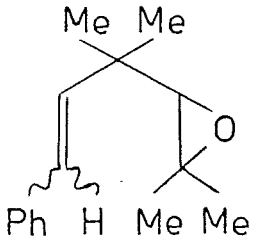

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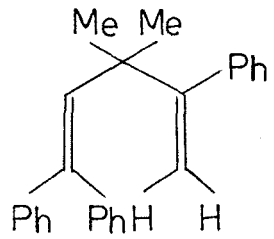

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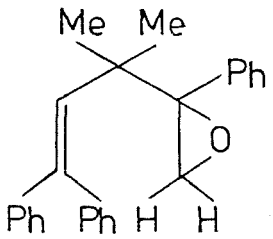

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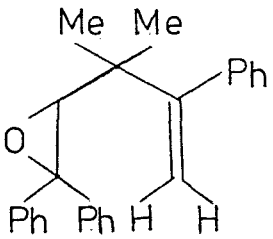

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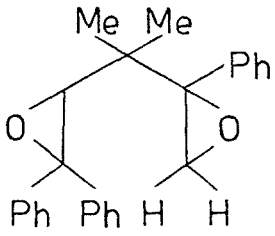

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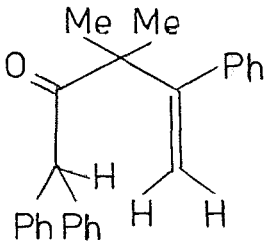

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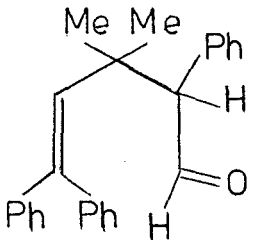

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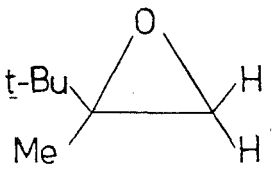

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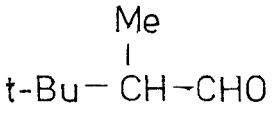

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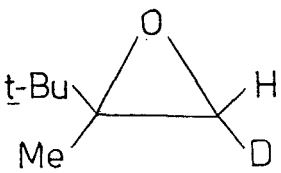

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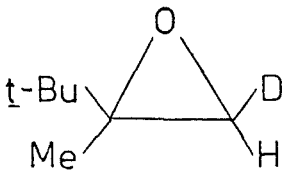

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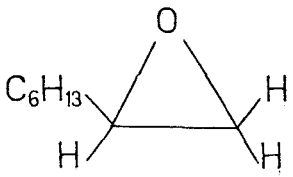

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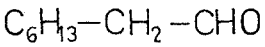

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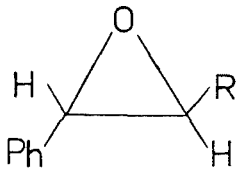

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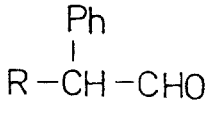
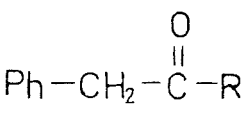


181

R = Me
Et
iso-Pr
t-Bu



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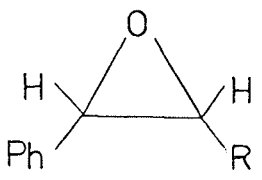
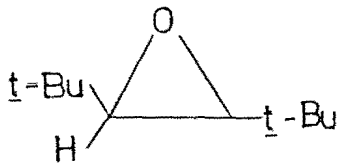


183

R = Me
Et
iso-Pr
t-Bu



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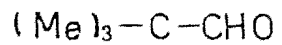

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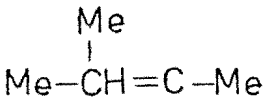

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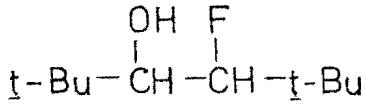

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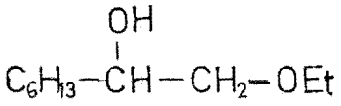

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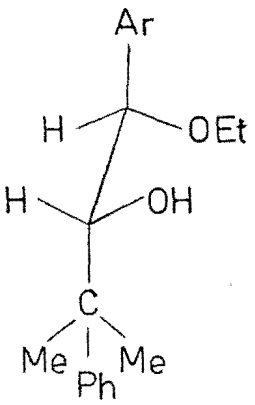
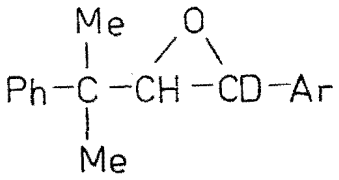


189

Ar: (a) Ph-H
(b) p-Ph-OMe
(c) p-Ph-Me
(d) p-Ph-Cl
(f) 3',4'-Ph-Cl_2



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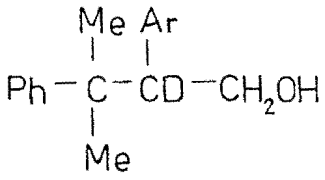
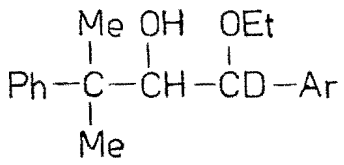


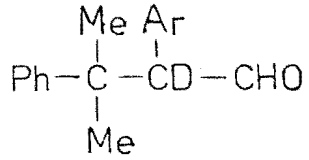
191

Ar: (a) Ph-H
(b) p-Ph-OMe
(d) p-Ph-Cl
(e) m-Ph-Cl



192

Ar: (a) Ph-H
(b) p-Ph-OMe
(d) p-Ph-Cl



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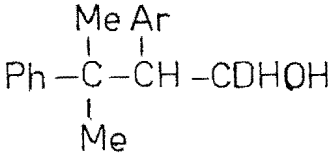
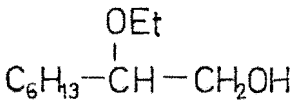


194

Ar: (a) Ph-H
(b) p-Ph-OMe
(d) p-Ph-Cl
(e) m-Ph-Cl



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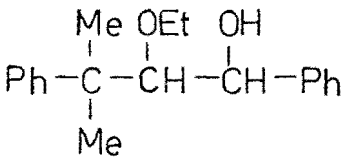

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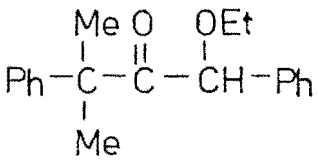

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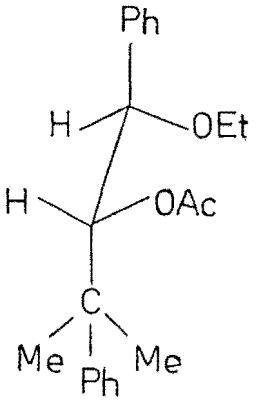

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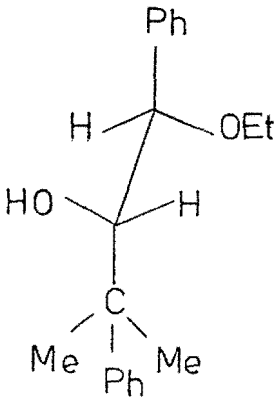

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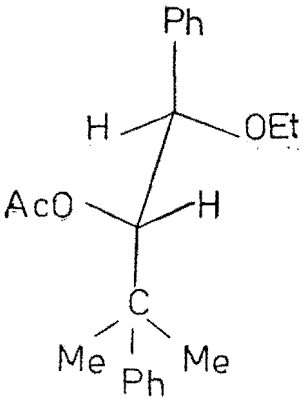

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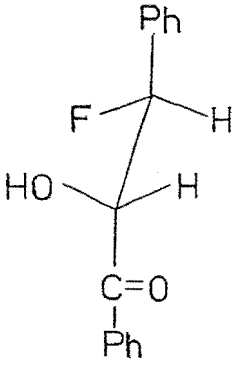

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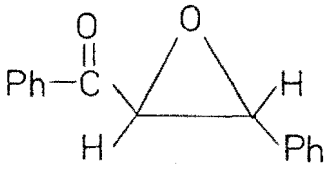

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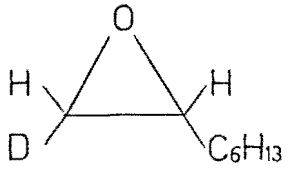

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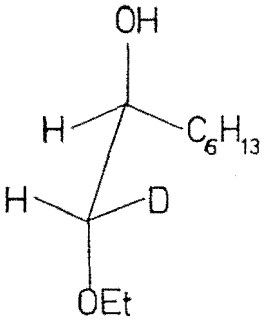

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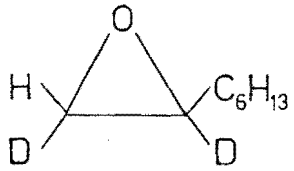

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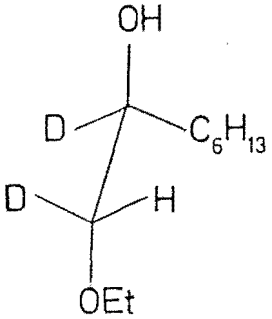

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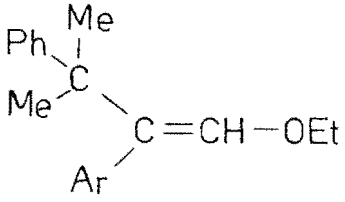

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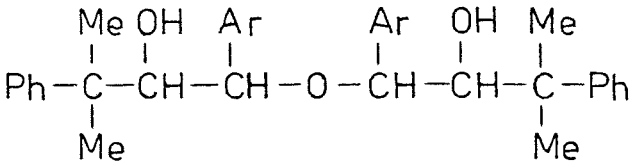
Ar: (a) Ph-H
(b) p-Ph-OMe
(d) p-Ph-Cl
(e) m-Ph-Cl



Ar: (a) Ph-H
(d) p-Ph-Cl

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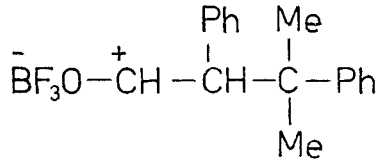

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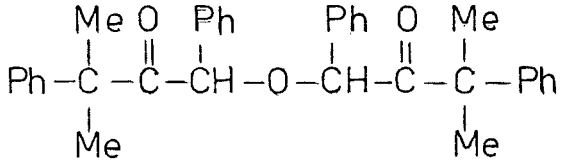

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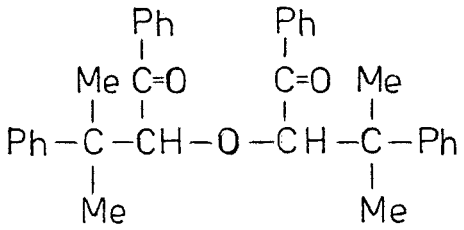

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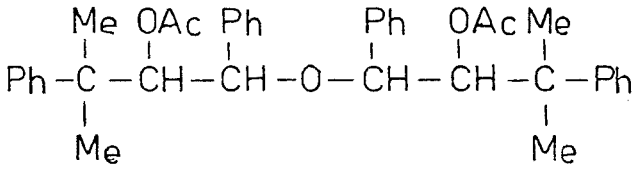

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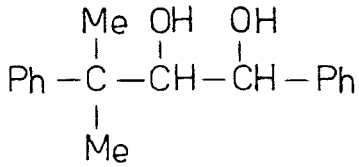

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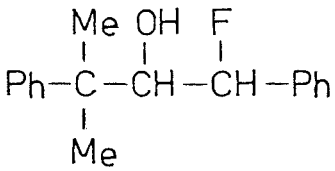

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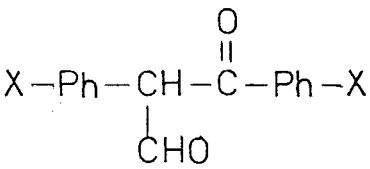

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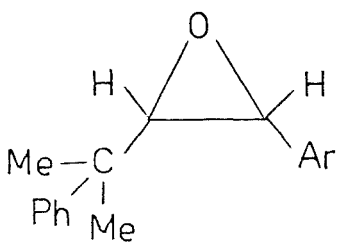

Ar: (b) p-Ph-OMe
(d) p-Ph-Cl
(e) m-Ph-Cl

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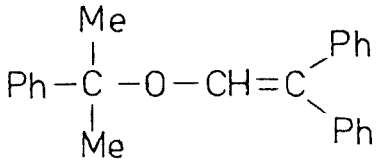

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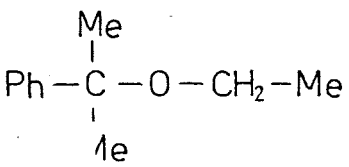

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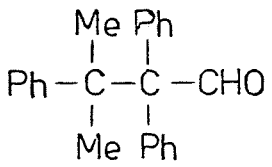

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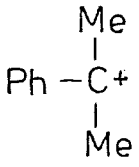

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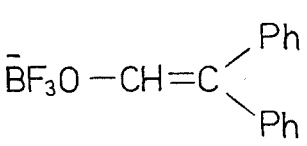

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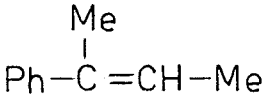

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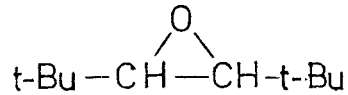

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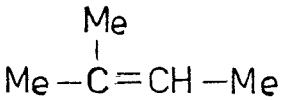

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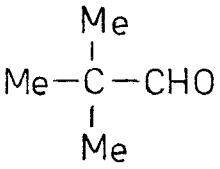

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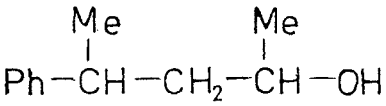

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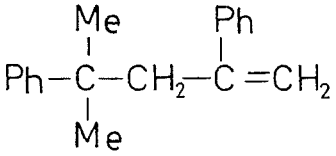

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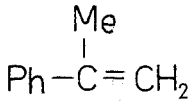

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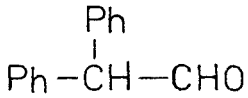

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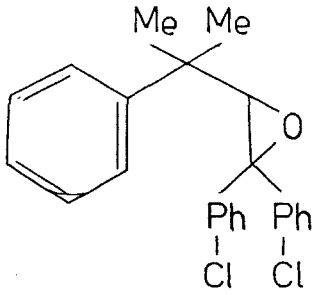

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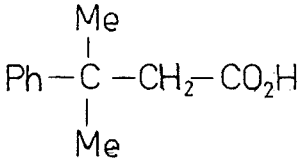

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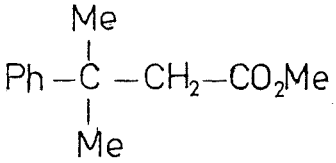

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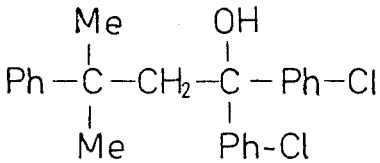

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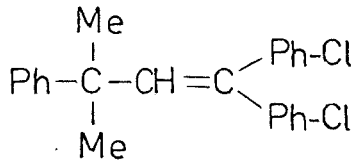

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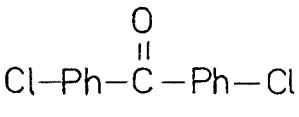

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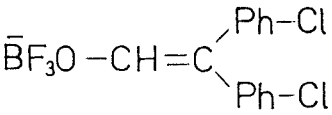

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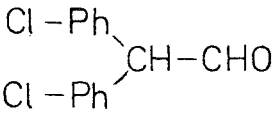

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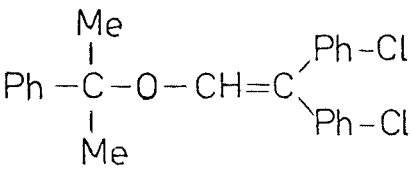

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